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**Rose et al.**

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(54) **ORGANIC MATERIALS ABLE TO DETECT ANALYTES**

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(73) Assignee: **Massachusetts Institute of Technology**, Cambridge, MA (US)

(\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

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**Related U.S. Application Data**

(63) Continuation of application No. 11/005,631, filed on Dec. 6, 2004, now Pat. No. 7,759,127.

(60) Provisional application No. 60/527,395, filed on Dec. 5, 2003.

(51) **Int. Cl.**  
**G01N 33/00** (2006.01)

(52) **U.S. Cl.** ..... **436/164**

(58) **Field of Classification Search** ..... 436/164  
See application file for complete search history.

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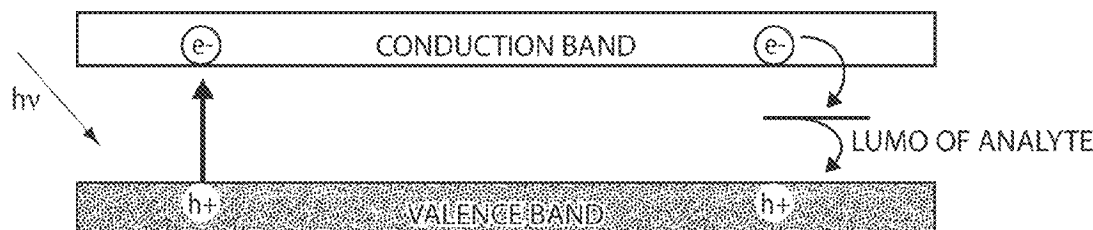
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(57) **ABSTRACT**

The present invention generally relates to polymers with lasing characteristics that allow the polymers to be useful in detecting analytes. In one aspect, the polymer, upon an interaction with an analyte, may exhibit a change in a lasing characteristic that can be determined in some fashion. For example, interaction of an analyte with the polymer may affect the ability of the polymer to reach an excited state that allows stimulated emission of photons to occur, which may be determined, thereby determining the analyte. In another aspect, the polymer, upon interaction with an analyte, may exhibit a change in stimulated emission that is at least 10 times greater with respect to a change in the spontaneous emission of the polymer upon interaction with the analyte. The polymer may be a conjugated polymer in some cases. In one set of embodiments, the polymer includes one or more hydrocarbon side chains, which may be parallel to the polymer backbone in some instances. In another set of embodiments, the polymer may include one or more pendant aromatic rings. In yet another set of embodiments, the polymer may be substantially encapsulated in a hydrocarbon. In still another set of embodiments, the polymer may be substantially resistant to photobleaching. In certain aspects, the polymer may be useful in the detection of explosive agents, such as 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT).

**29 Claims, 39 Drawing Sheets**



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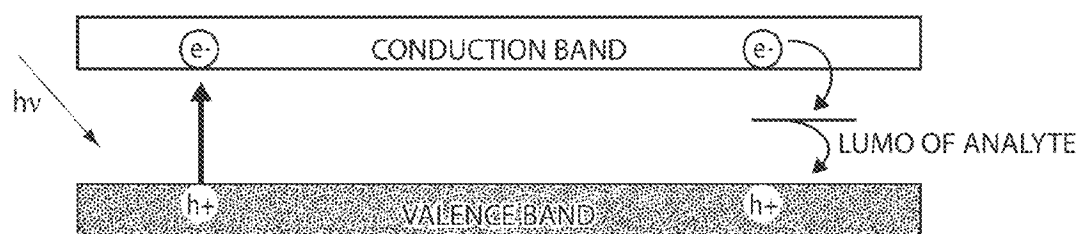


Fig. 1

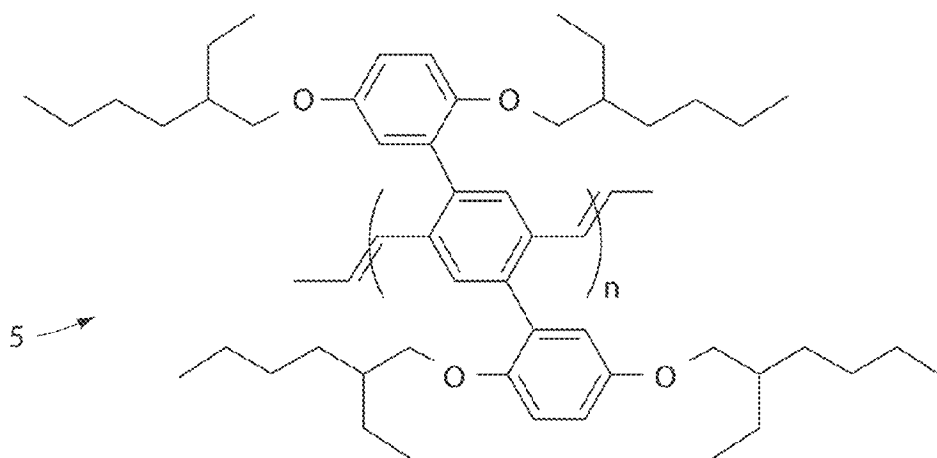


Fig. 2

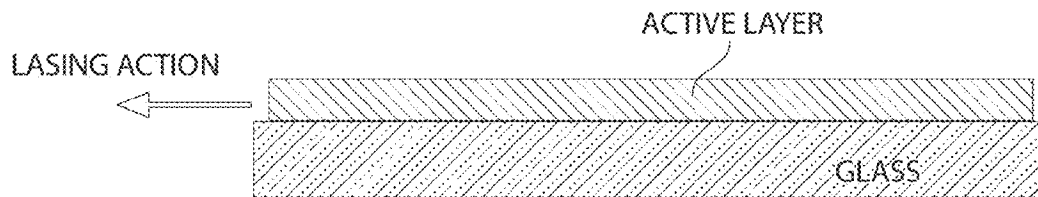


Fig. 3A

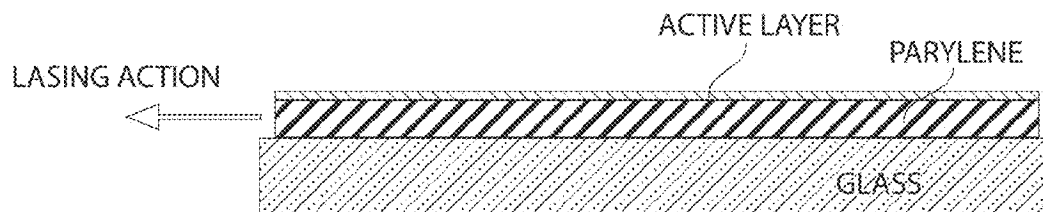


Fig. 3B

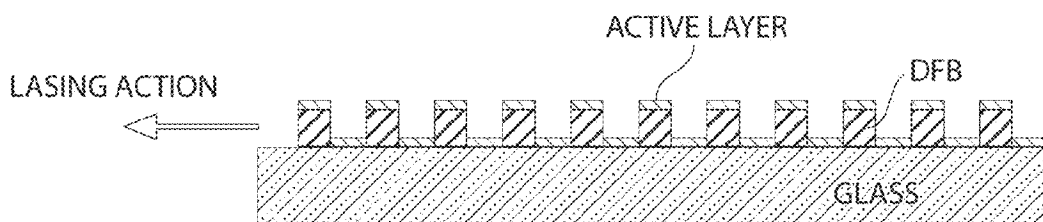


Fig. 3C

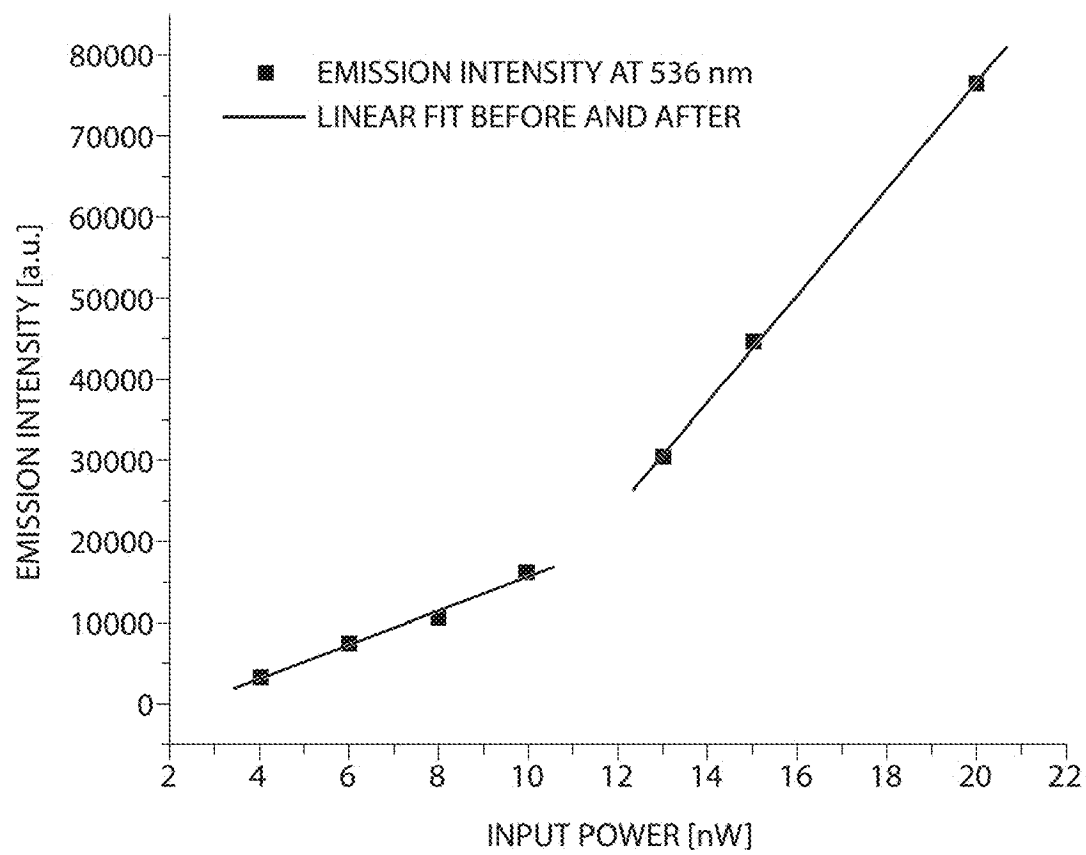


Fig. 4

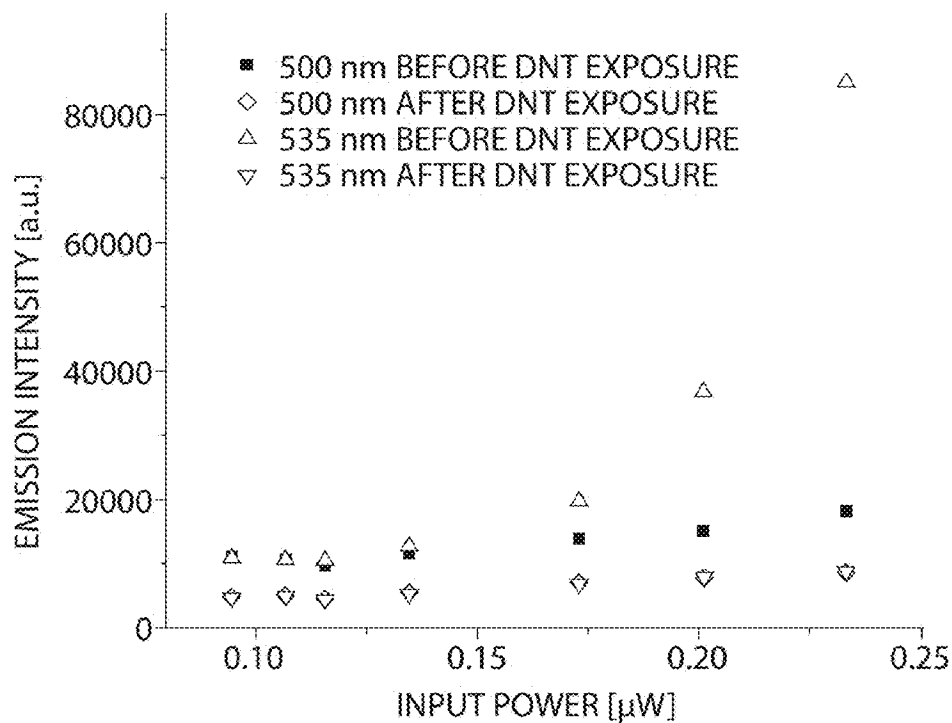


Fig. 5A

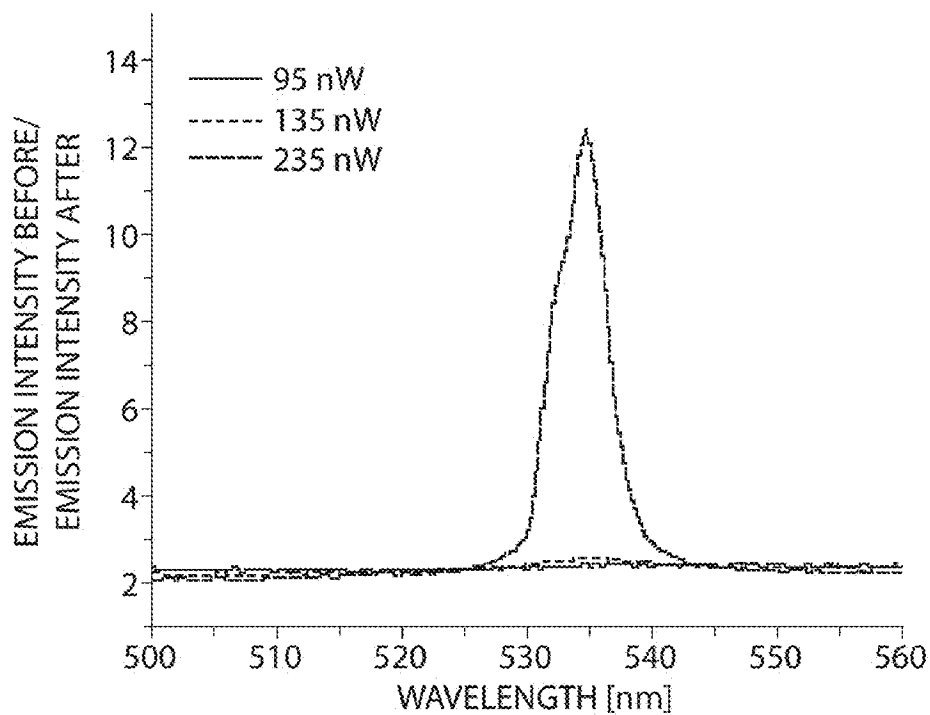


Fig. 5B

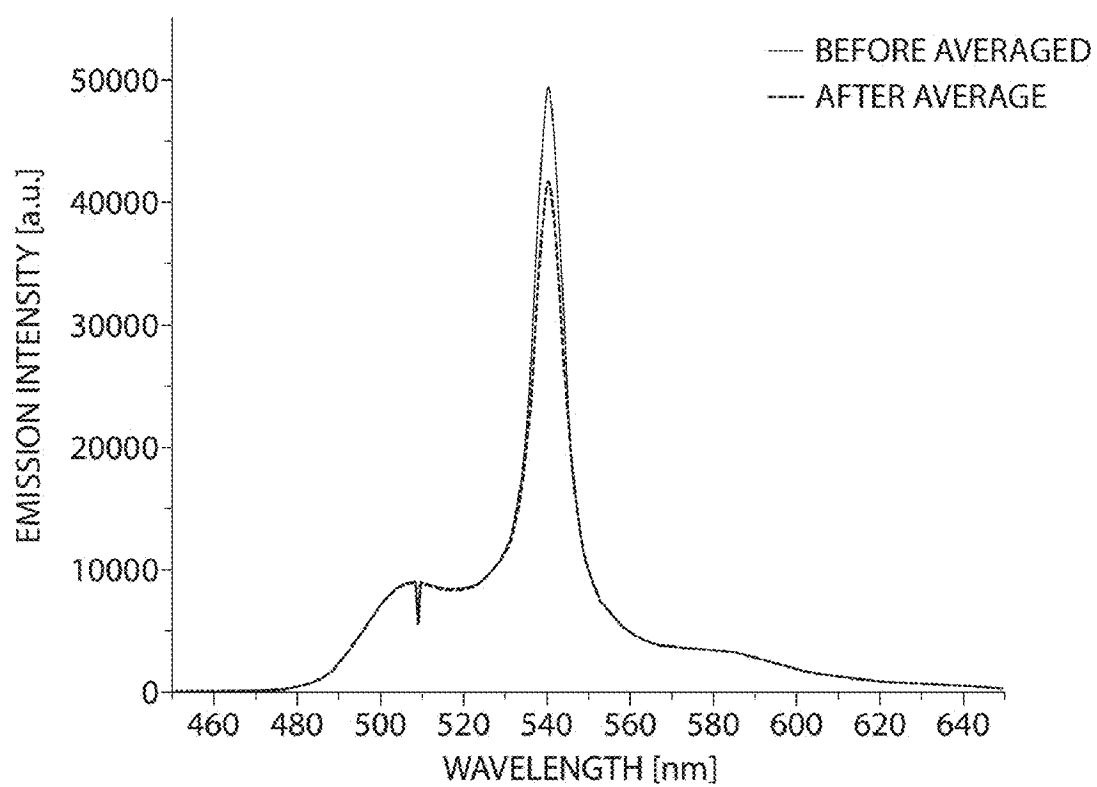


Fig. 6

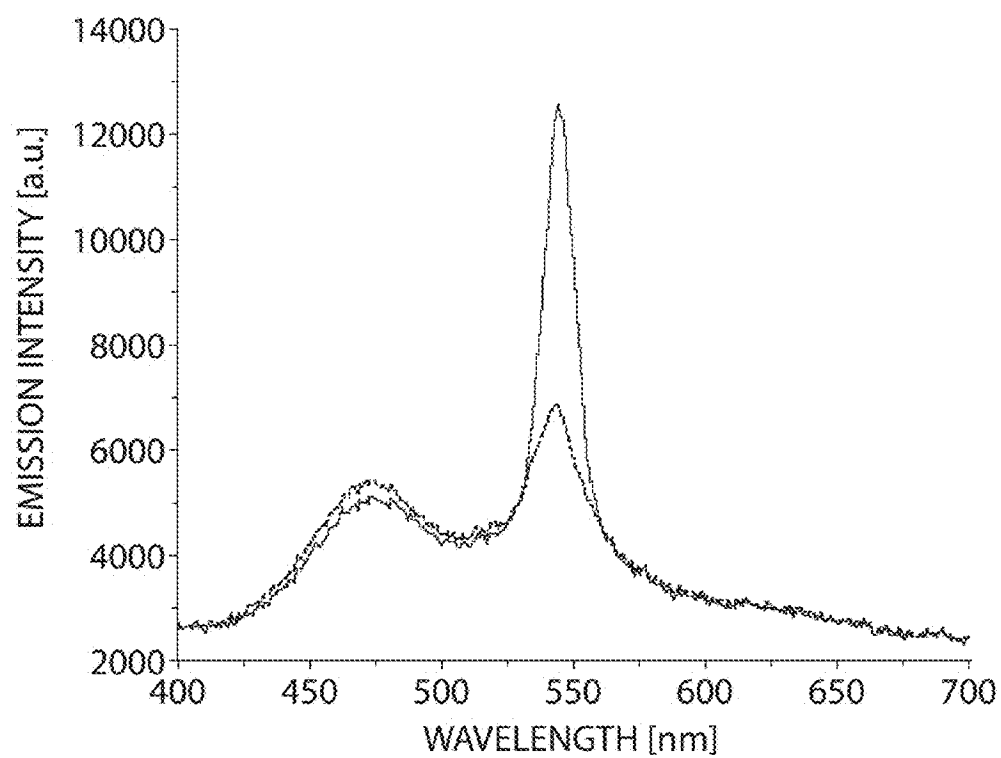


Fig. 7

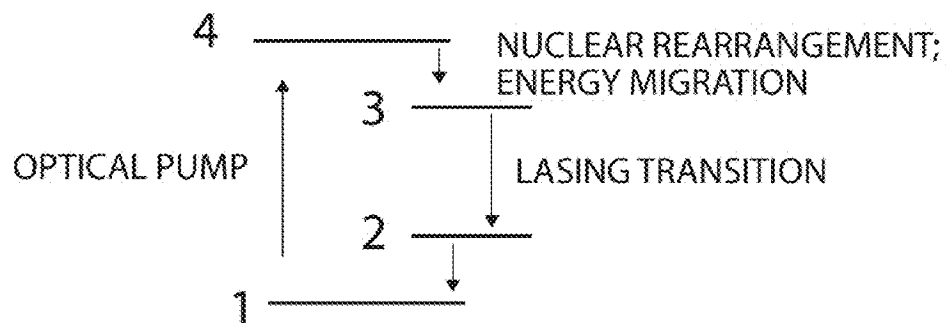


Fig. 8



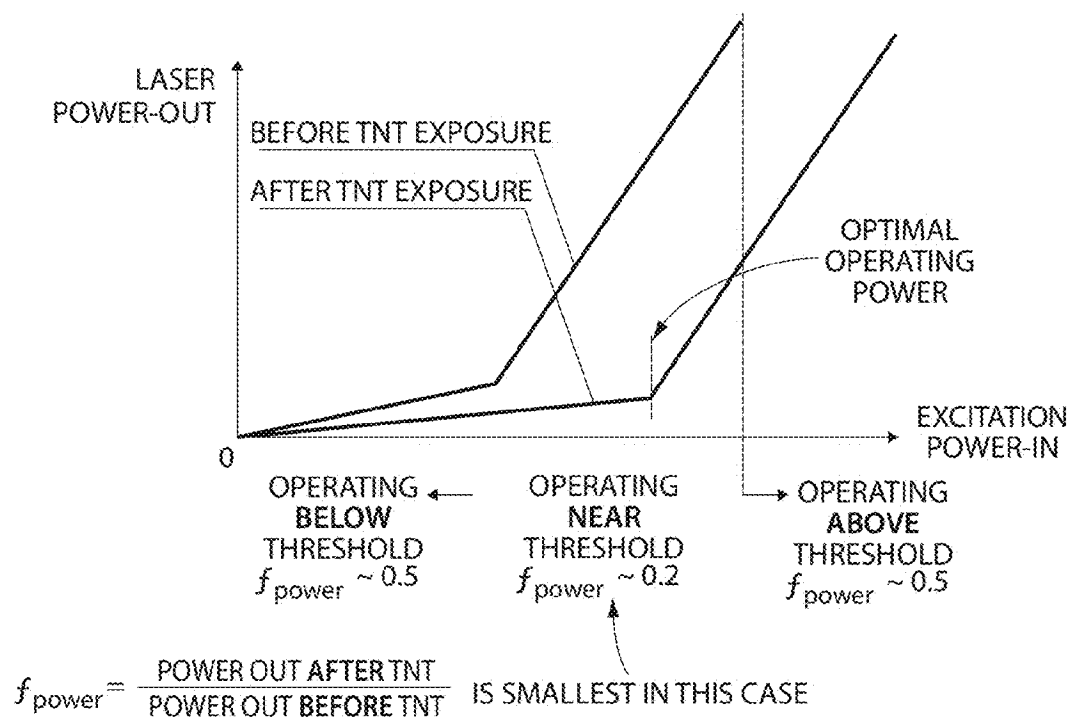


Fig. 9

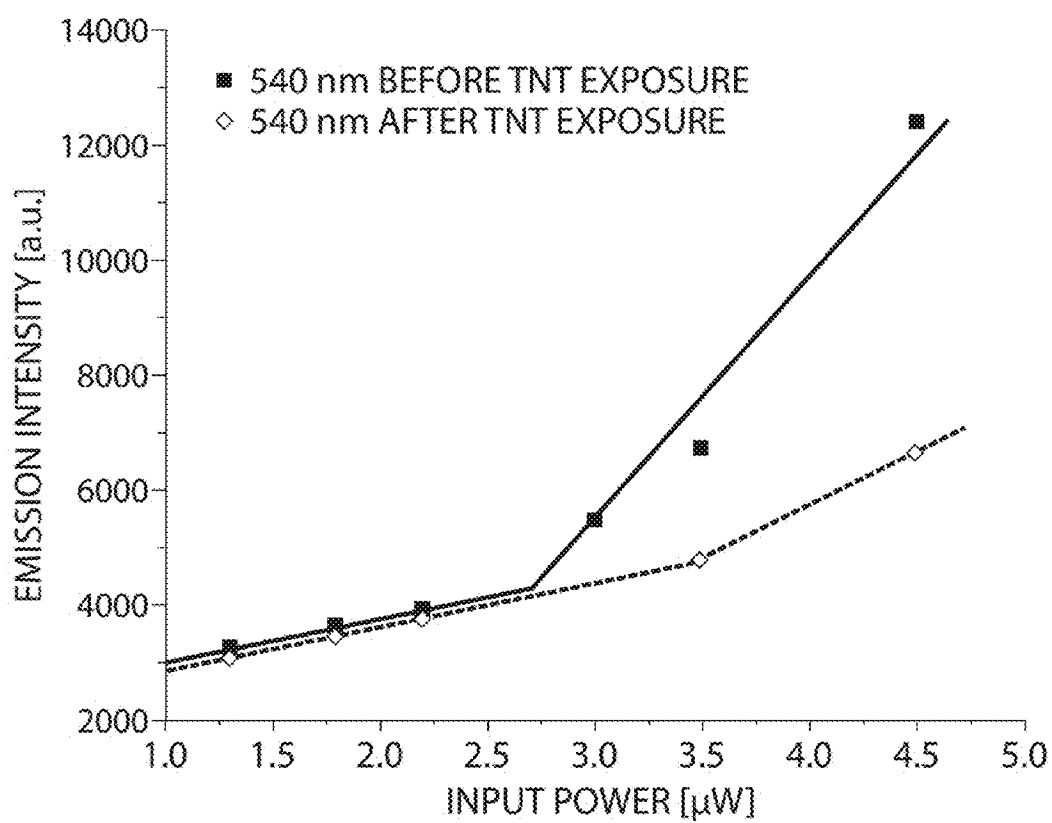


Fig. 10

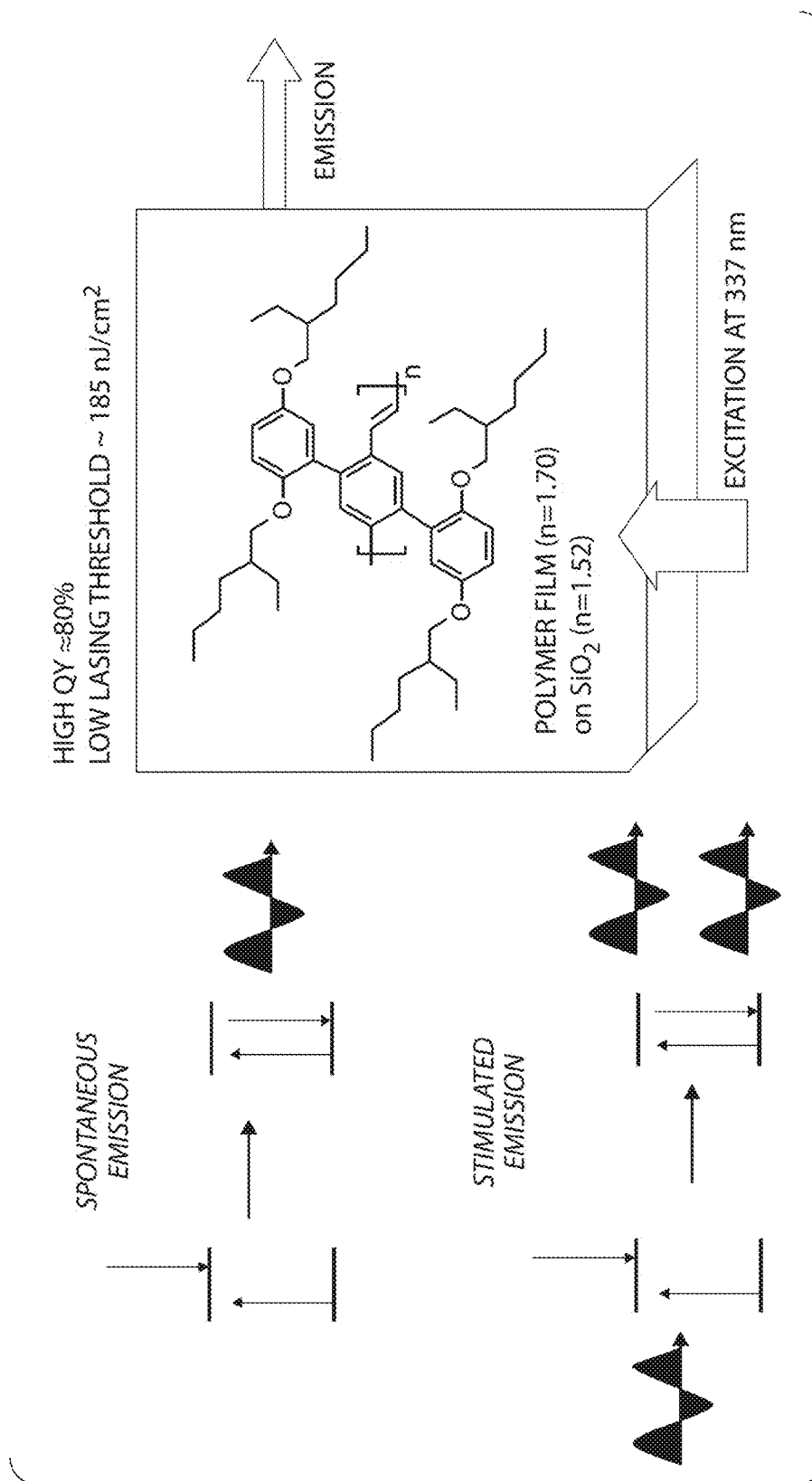


Fig. 11

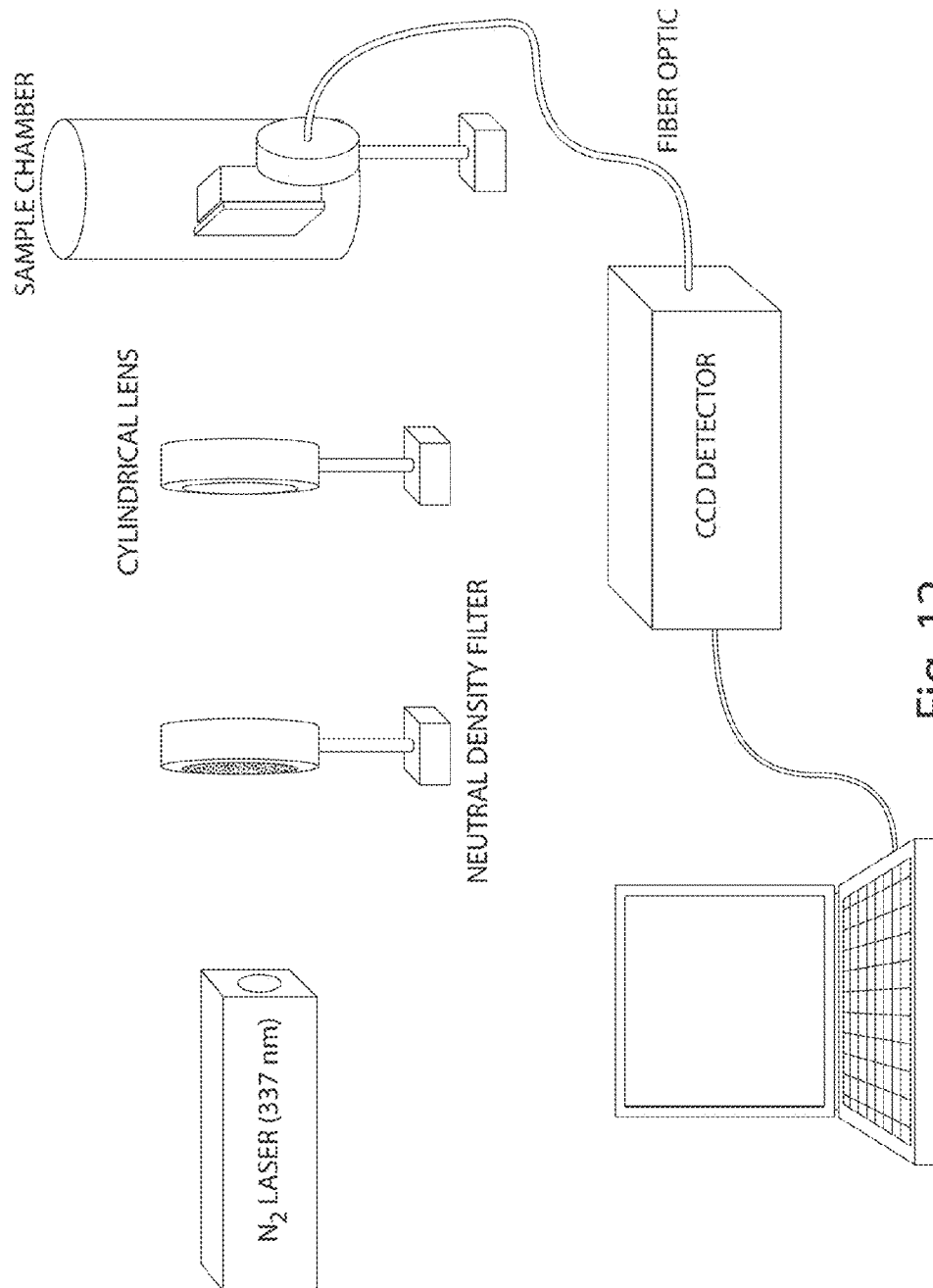
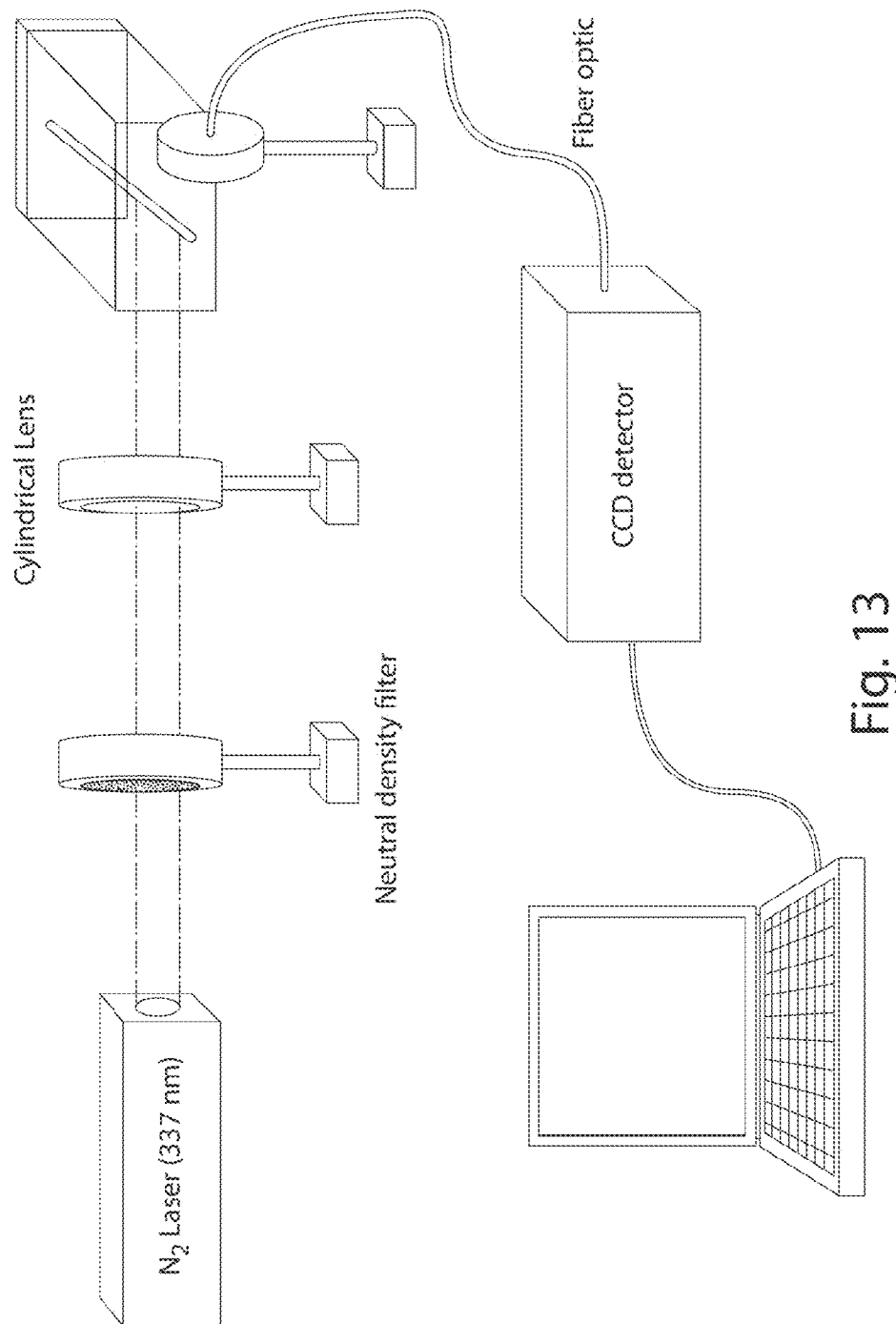


Fig. 12



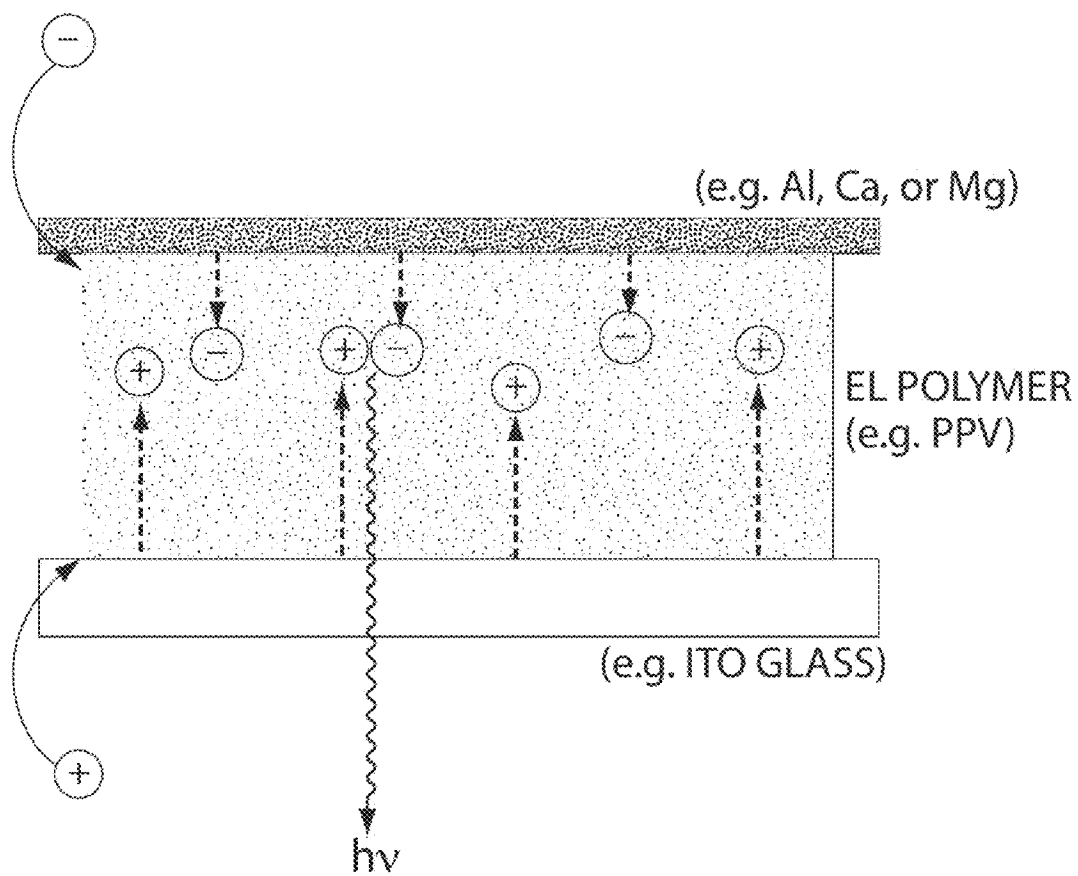


Fig. 14

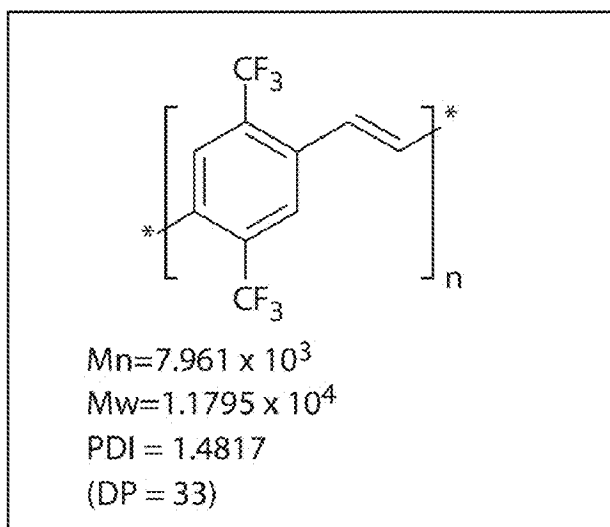


Fig. 15A

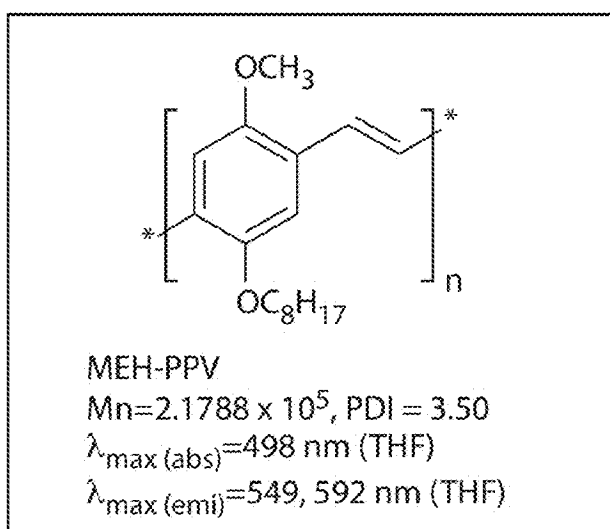


Fig. 15B

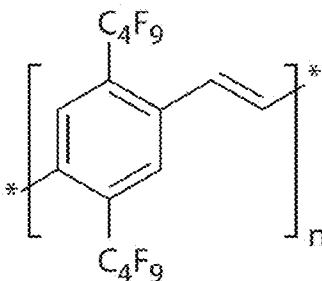


Fig. 15C

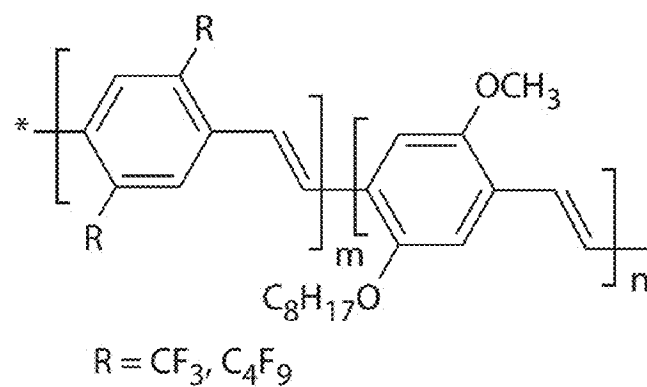


Fig. 15D

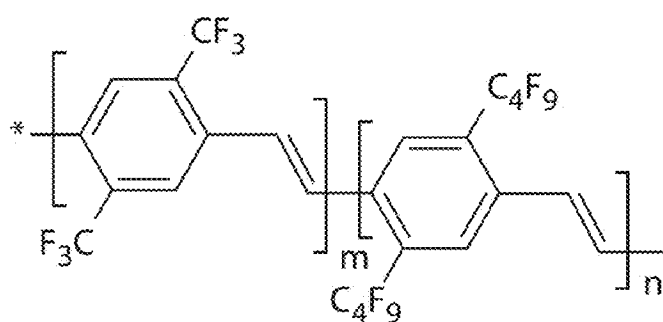


Fig. 15E

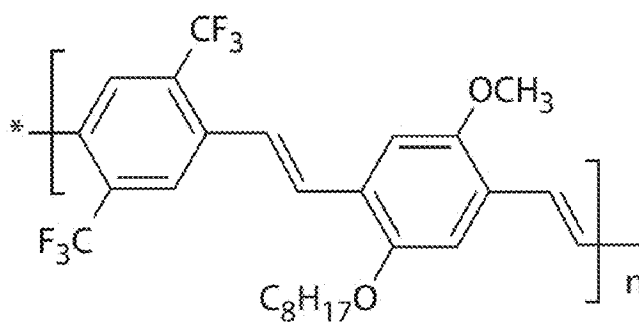


Fig. 15F



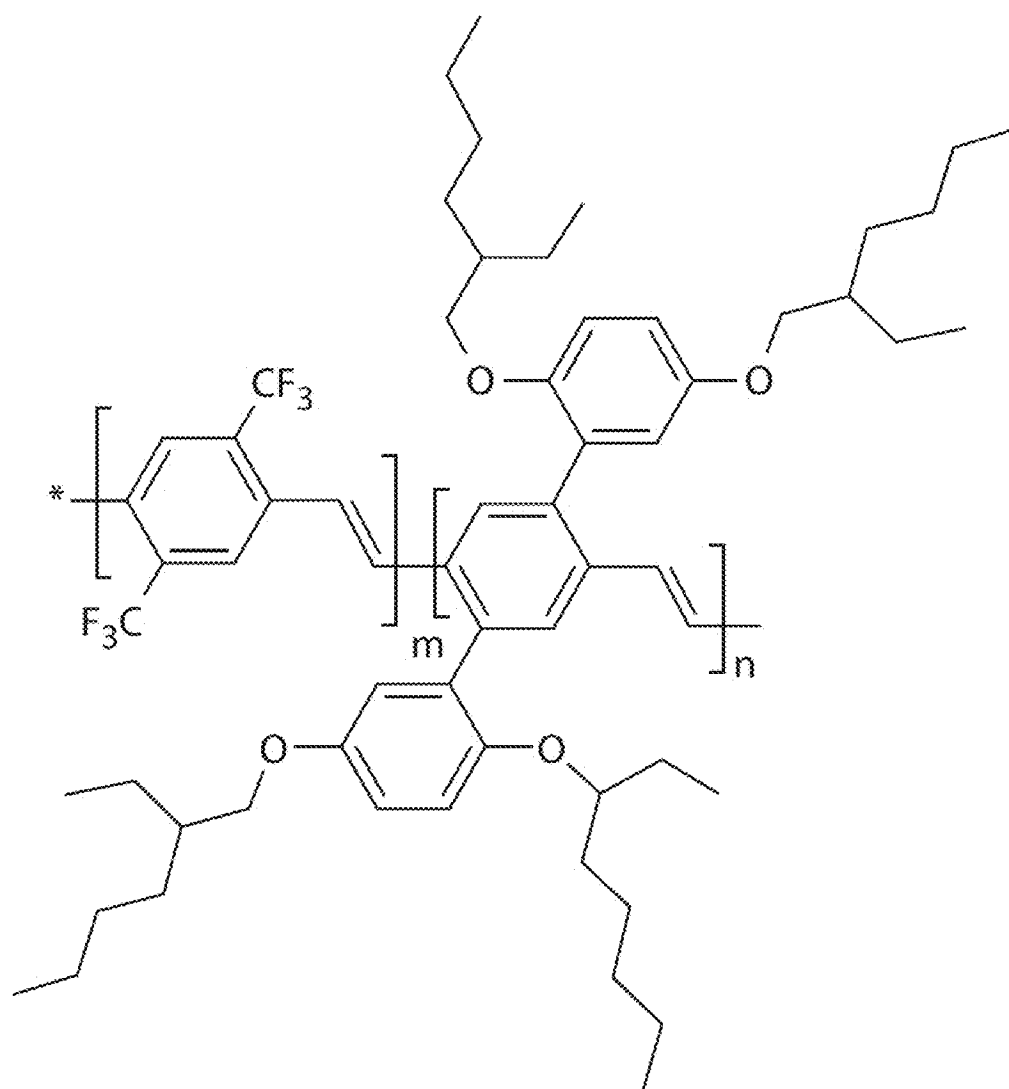


Fig. 15G

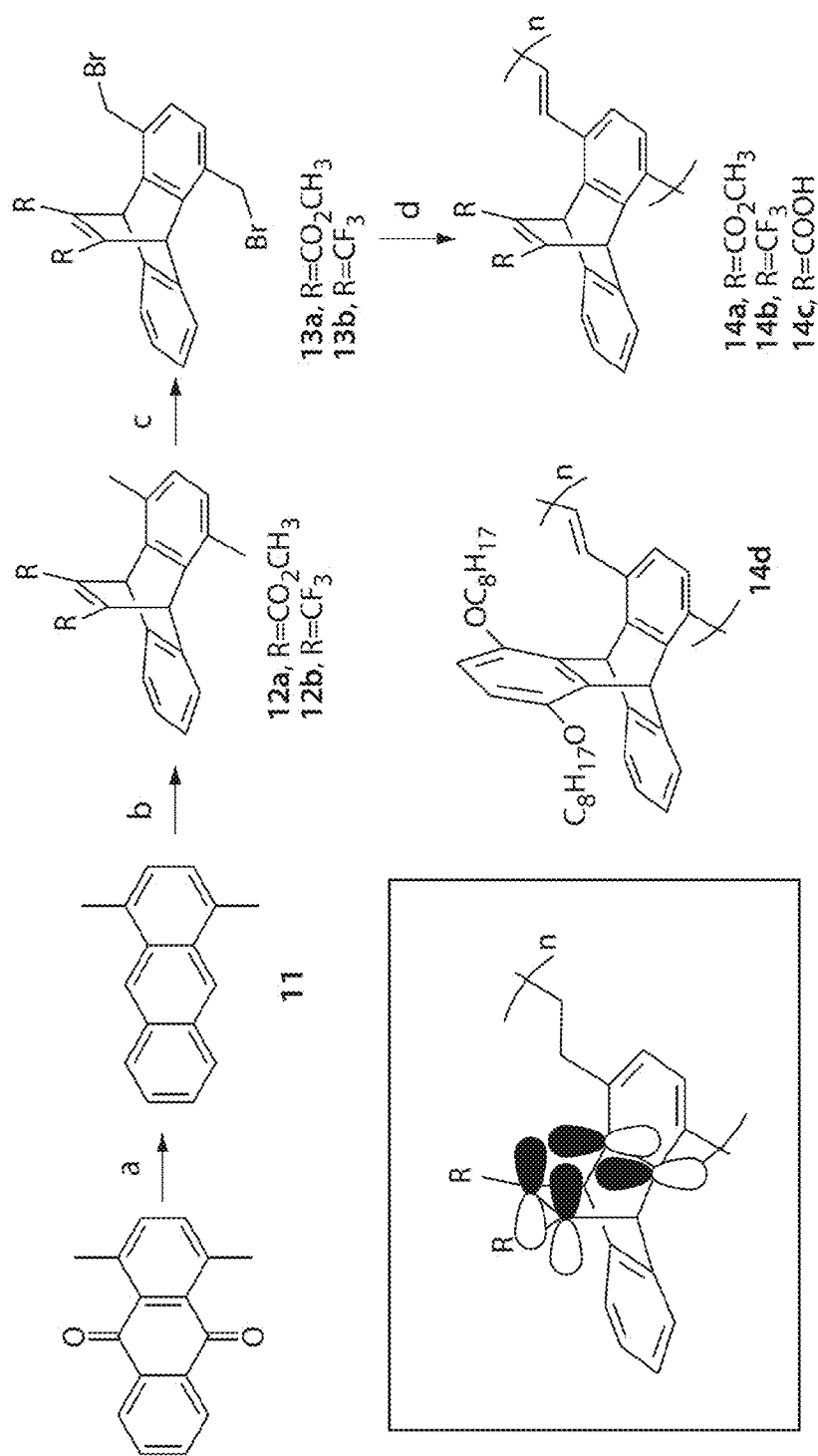
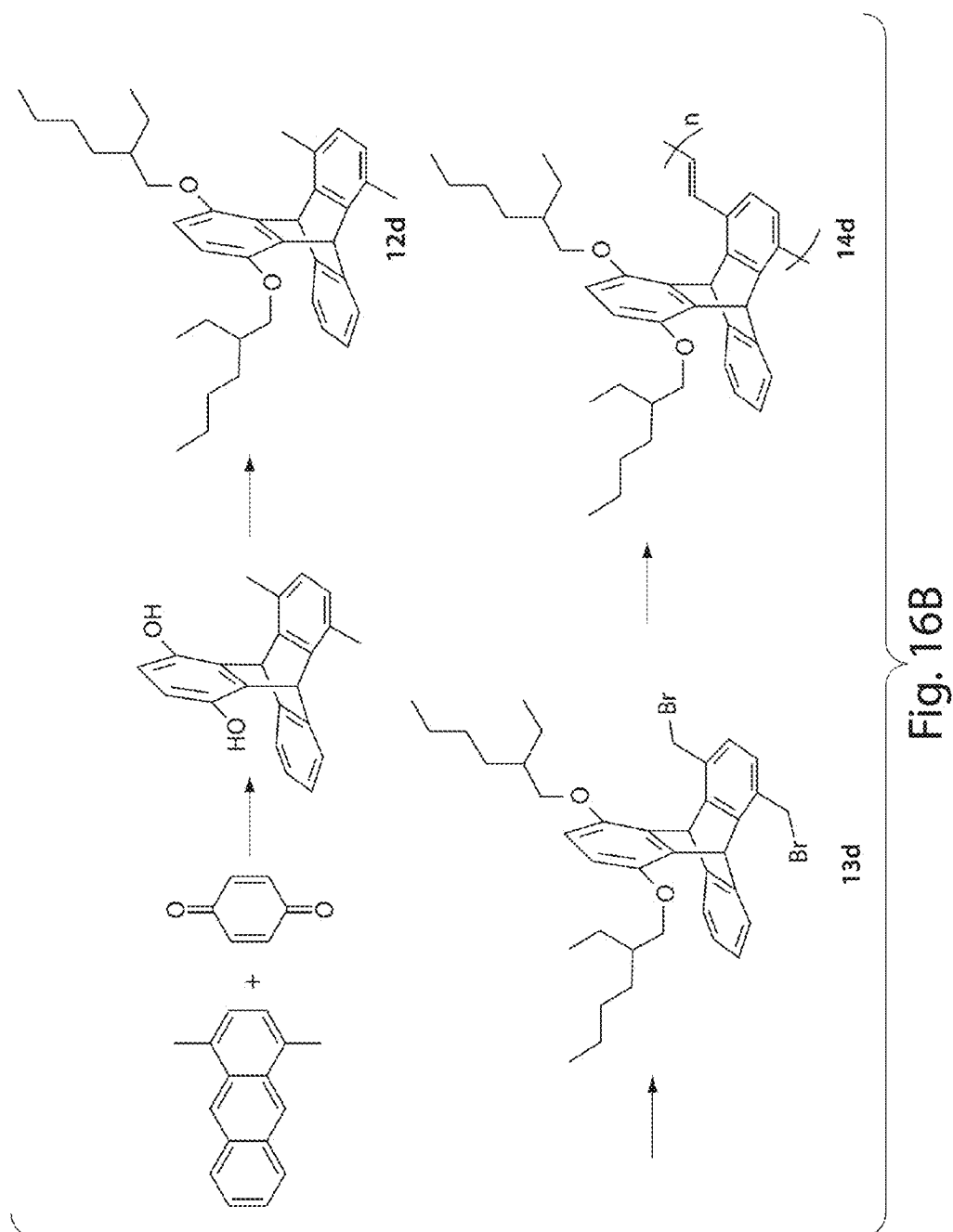


Fig. 16A



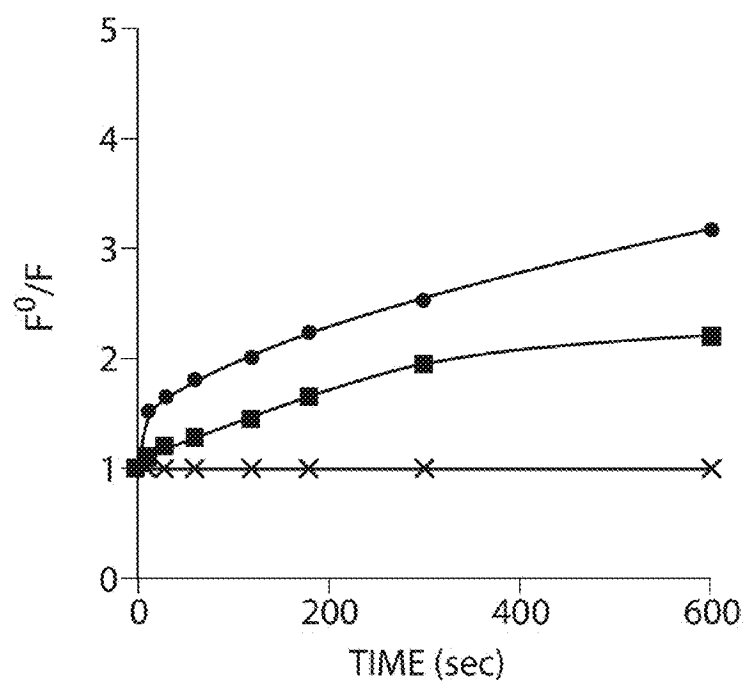


Fig. 17A

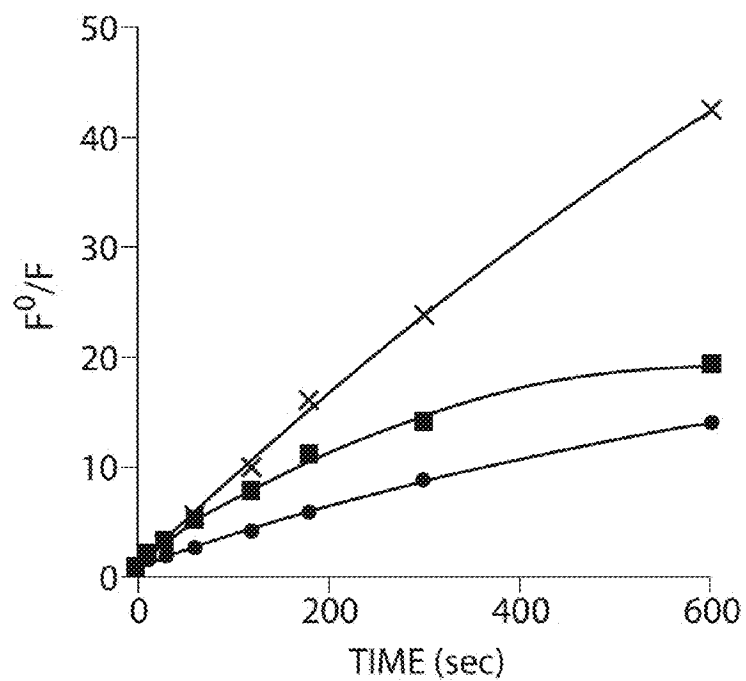


Fig. 17B

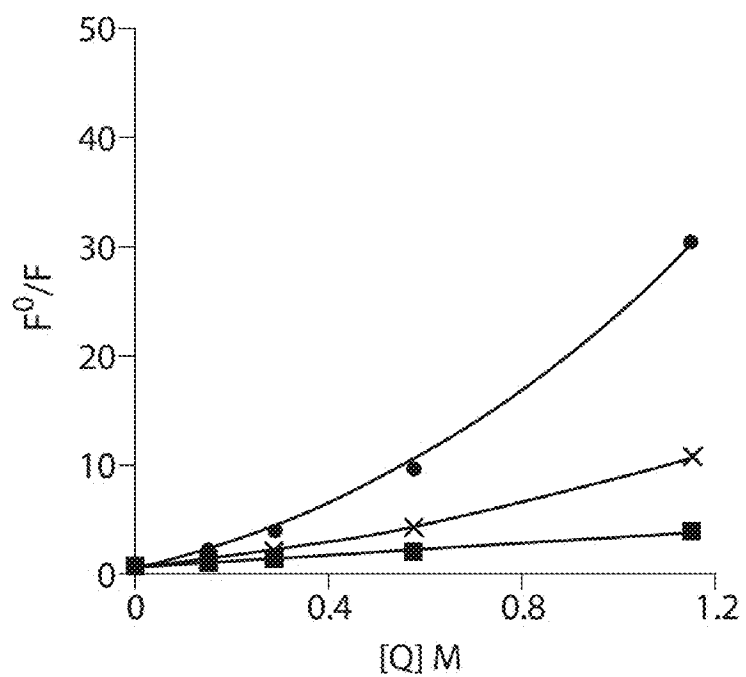


Fig. 17C

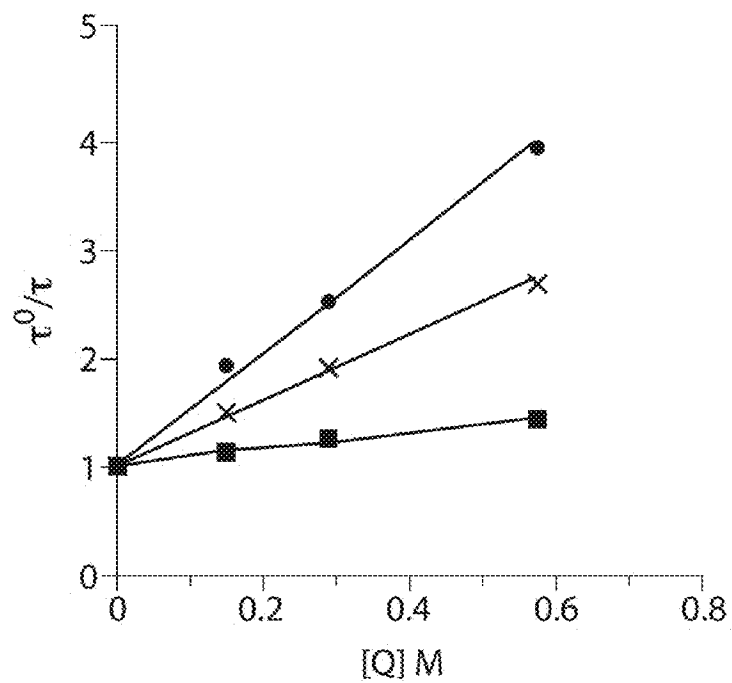


Fig. 17D

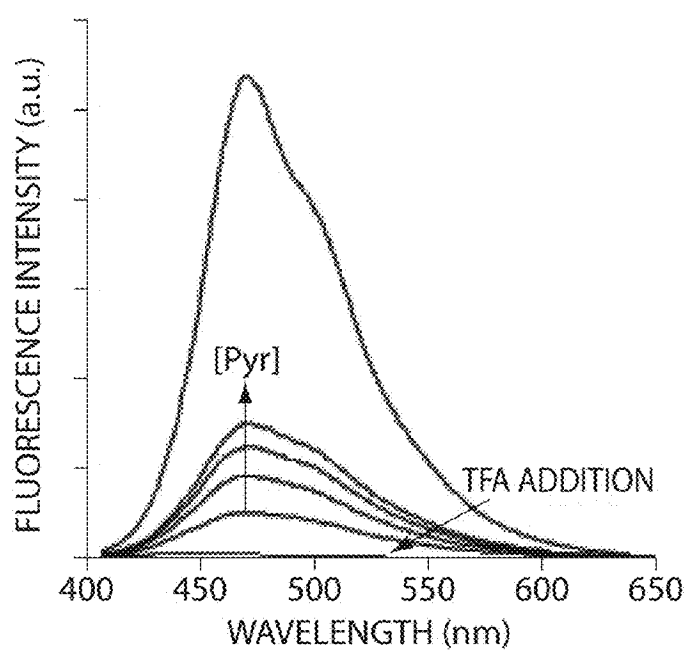


Fig. 18A

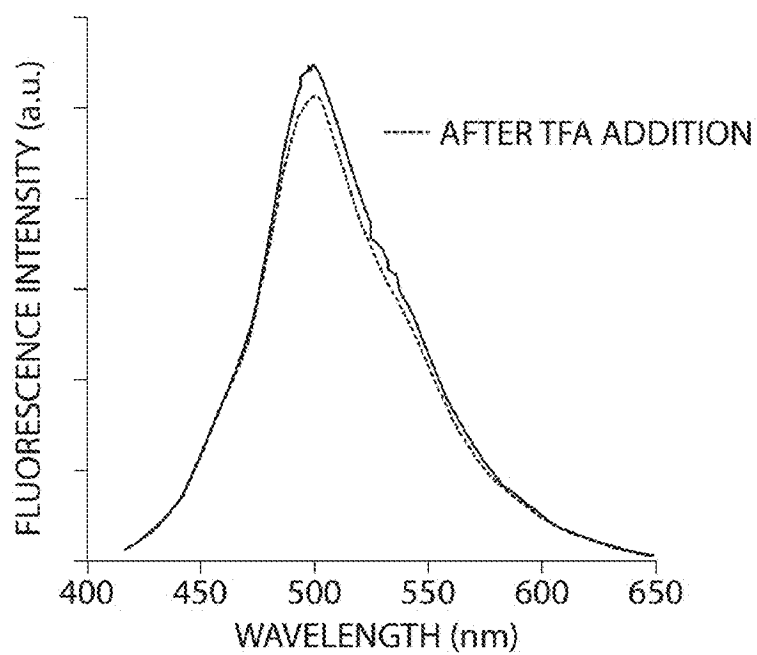


Fig. 18B

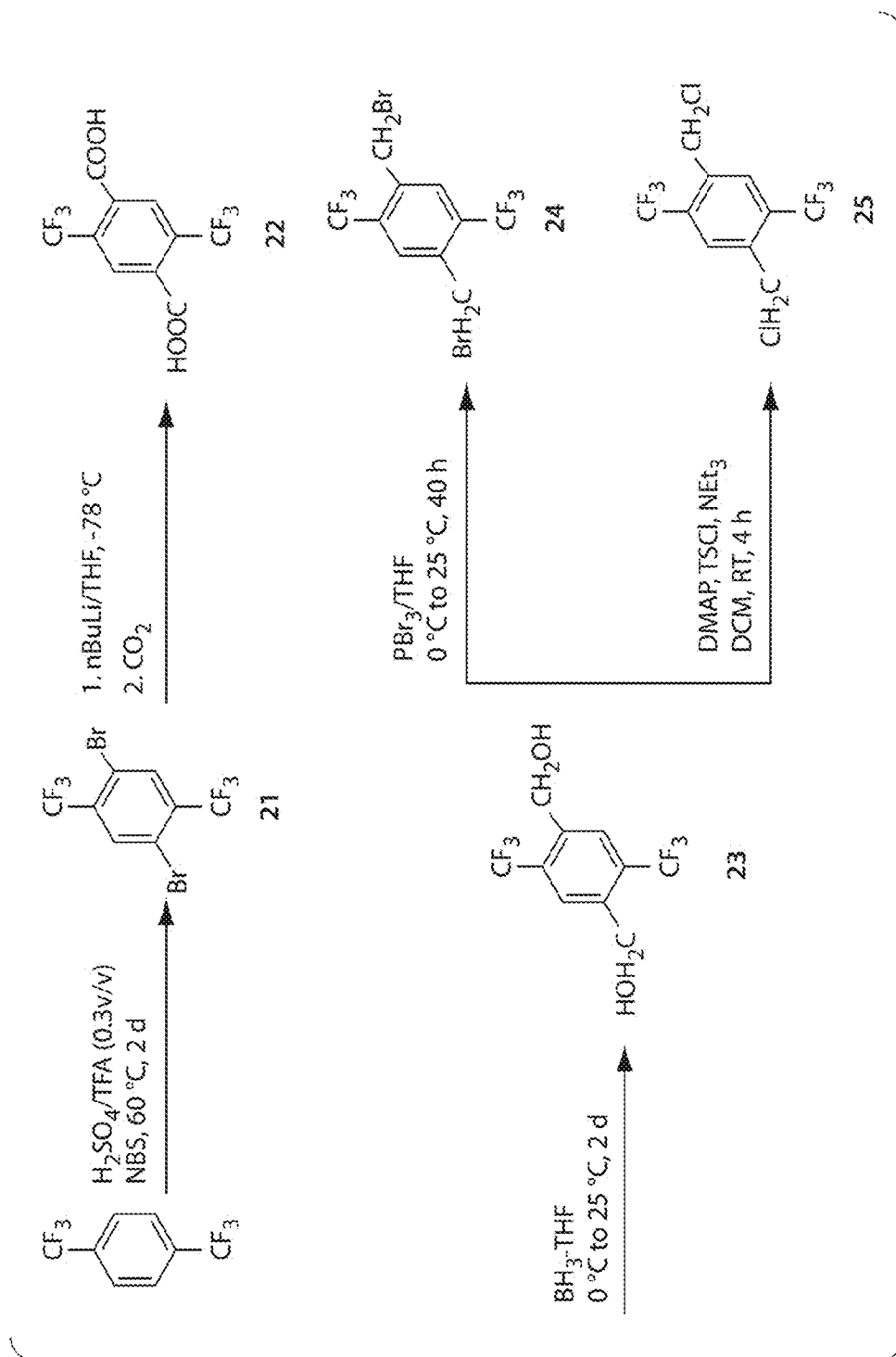


Fig. 19A

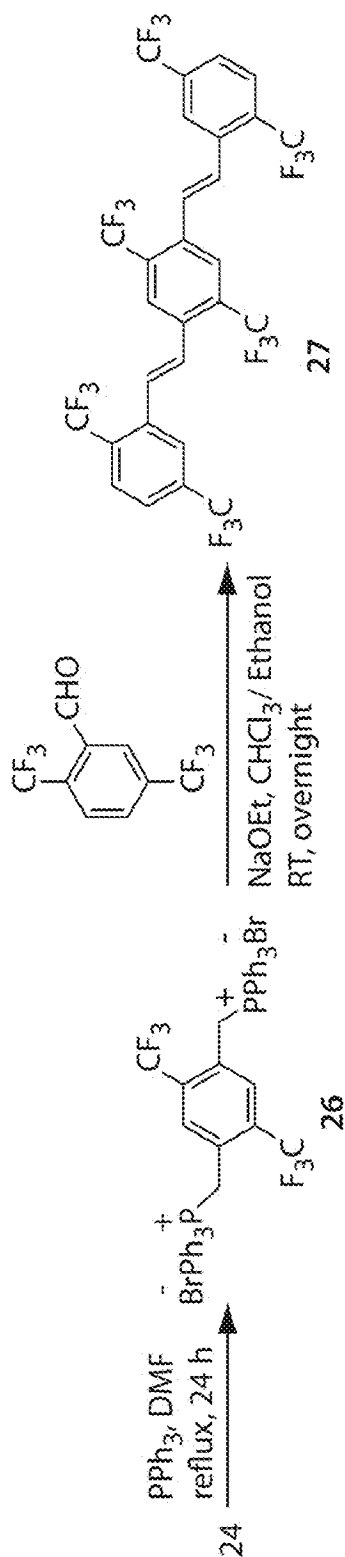
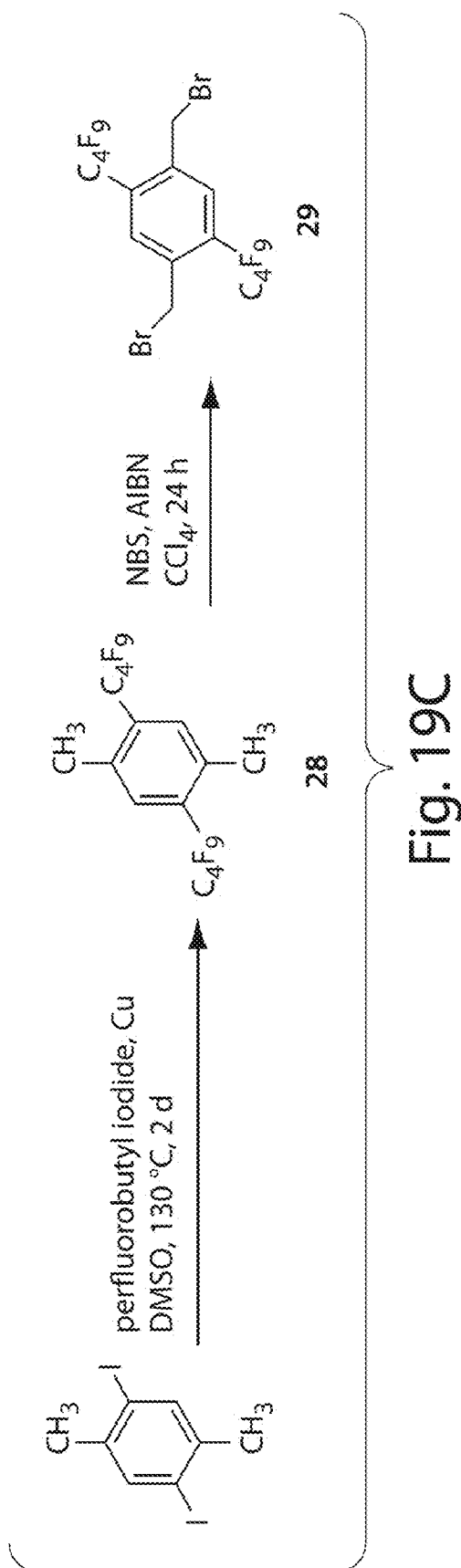


Fig. 19B





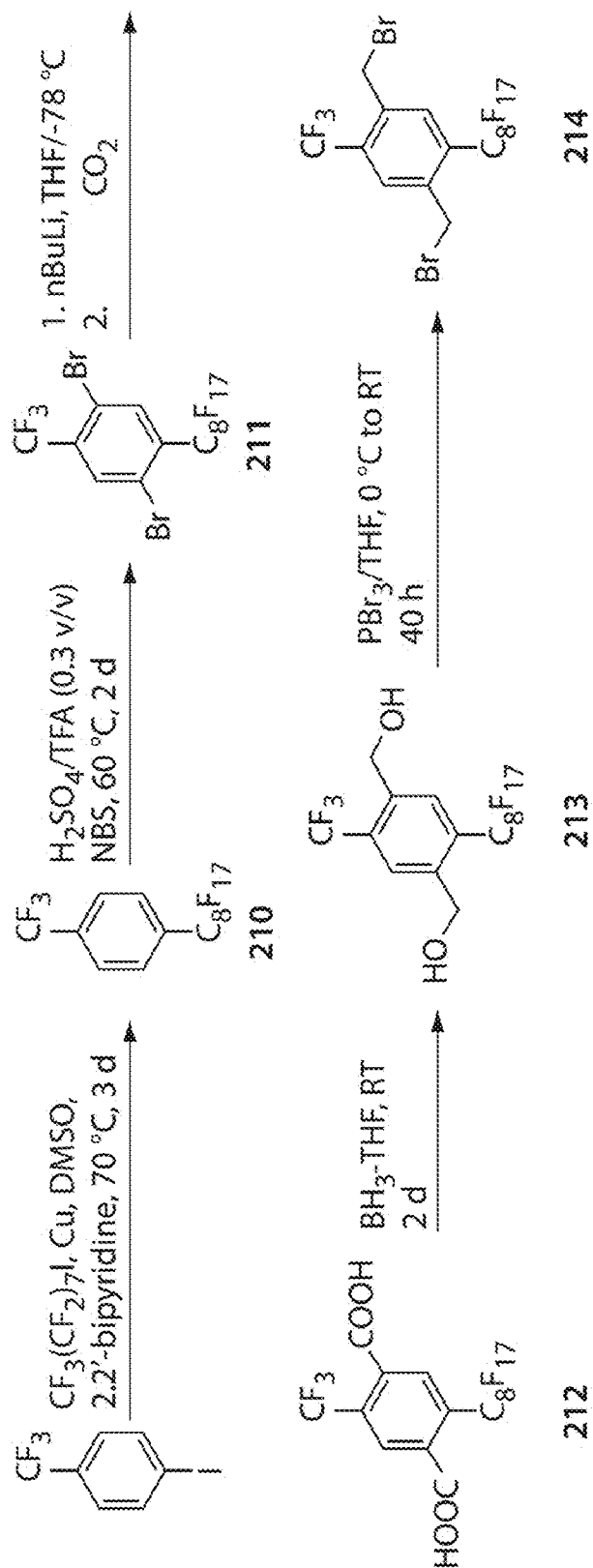
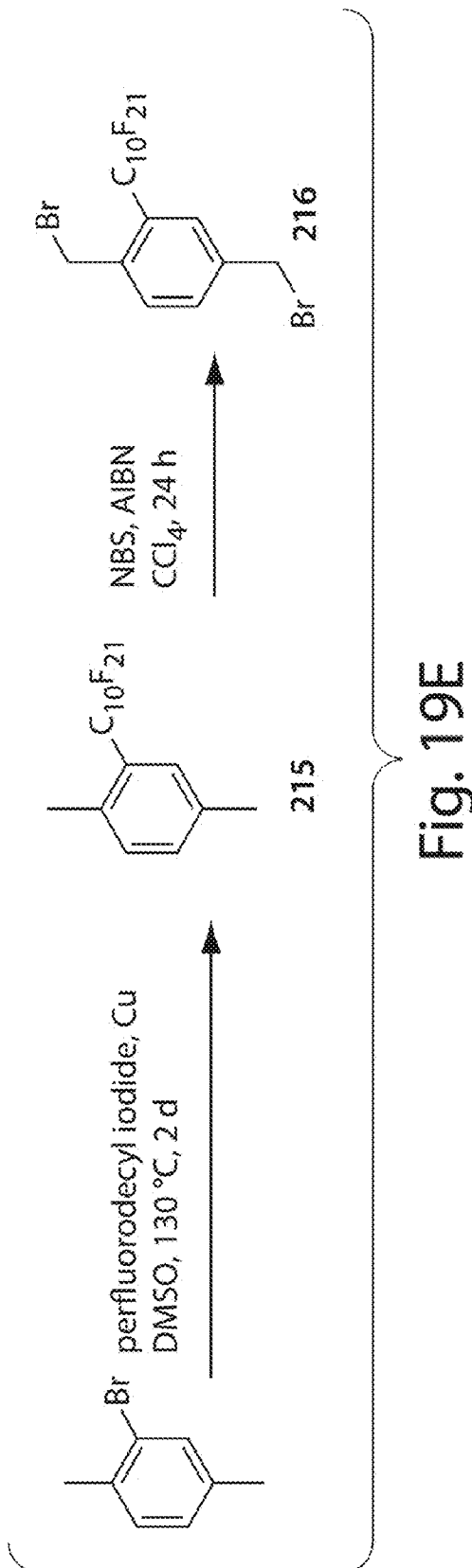
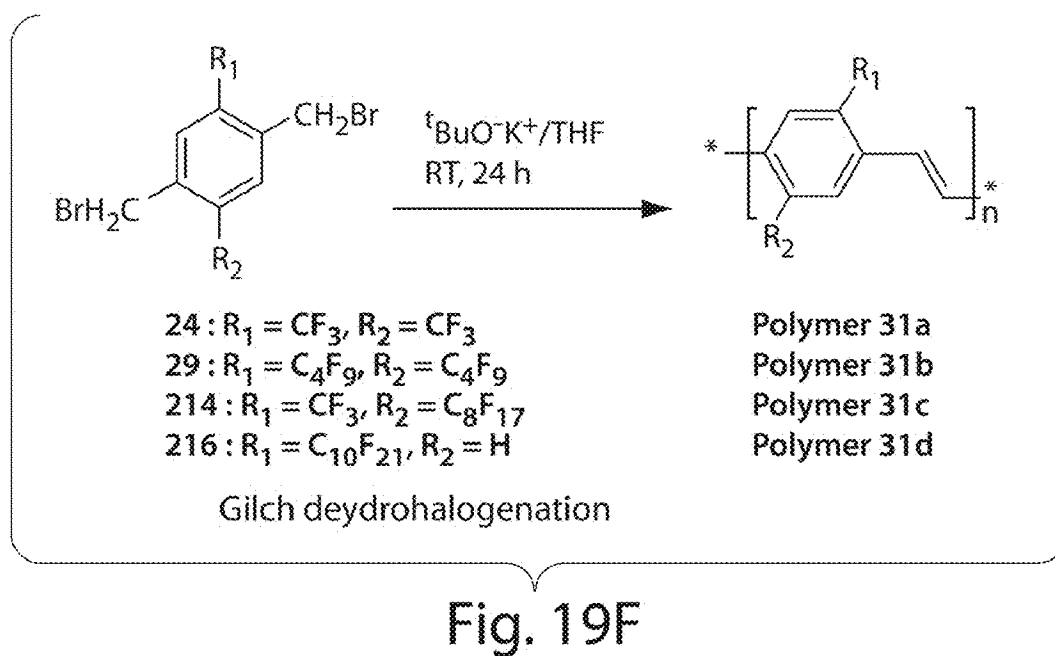
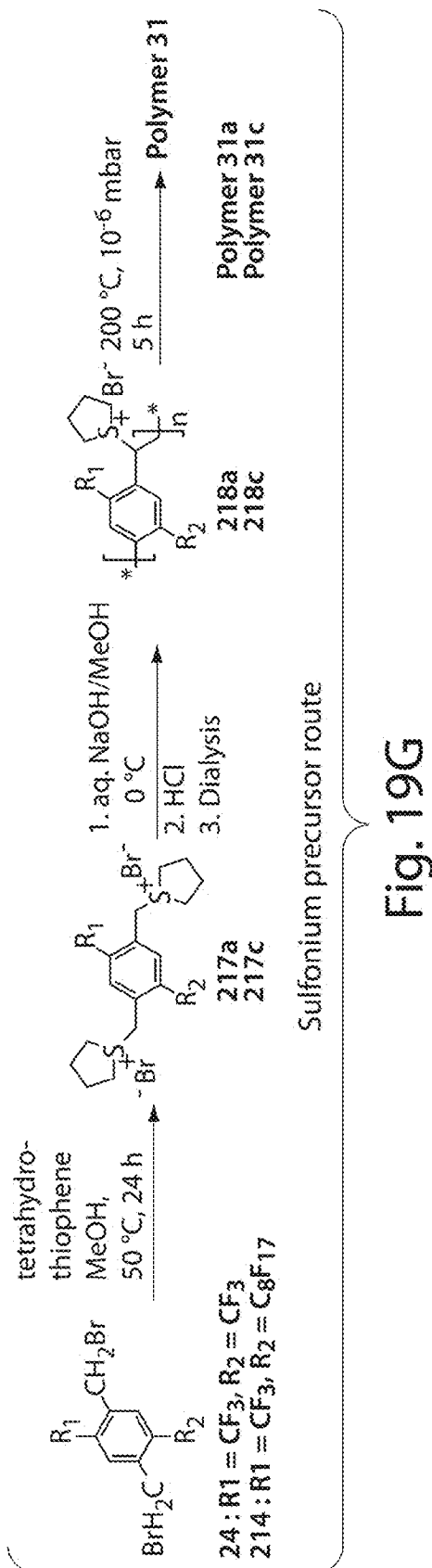
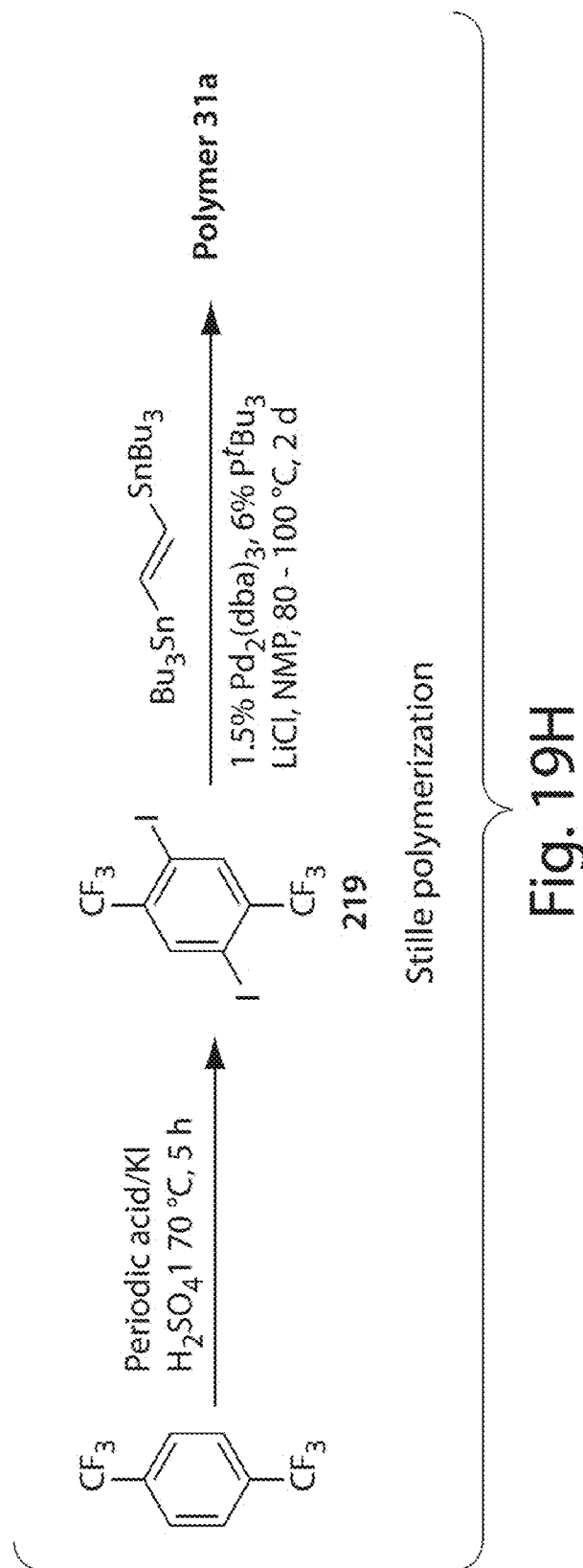


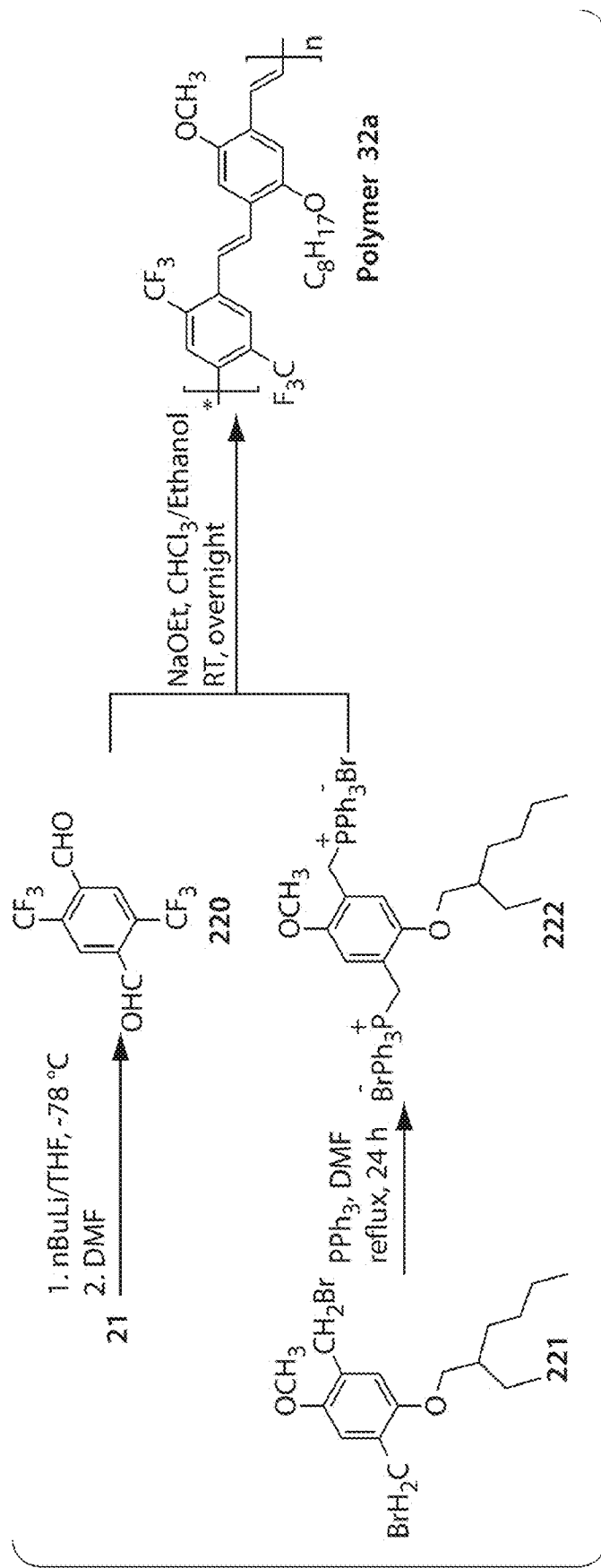
Fig. 19D











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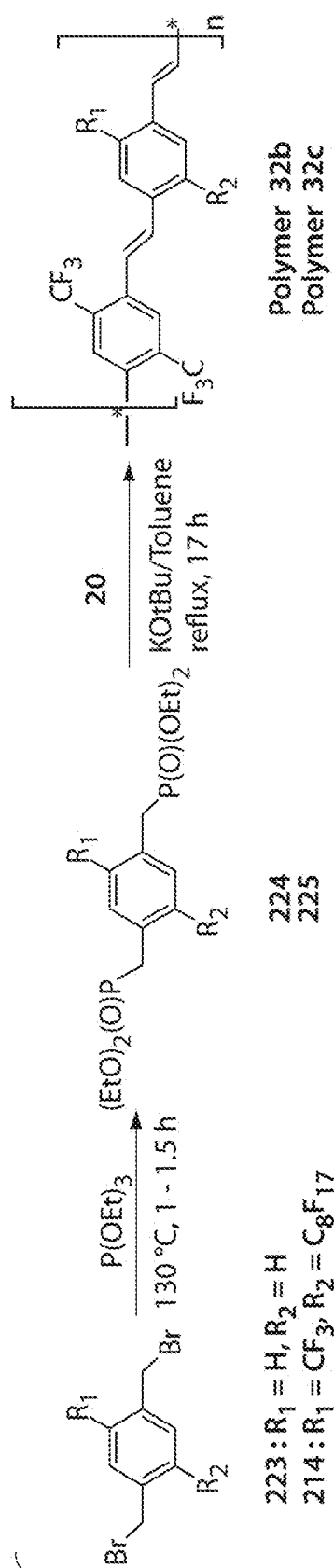


Fig. 19J



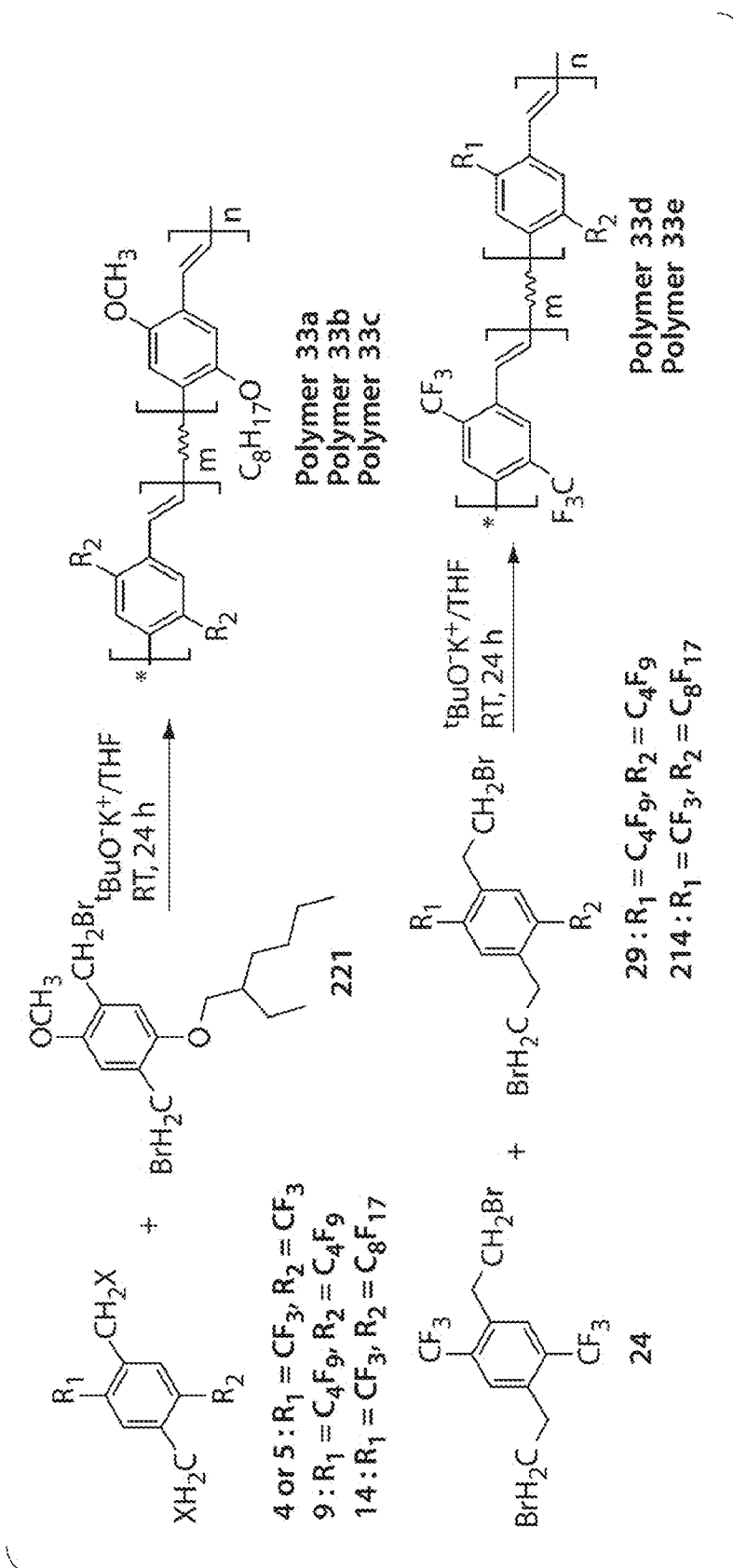
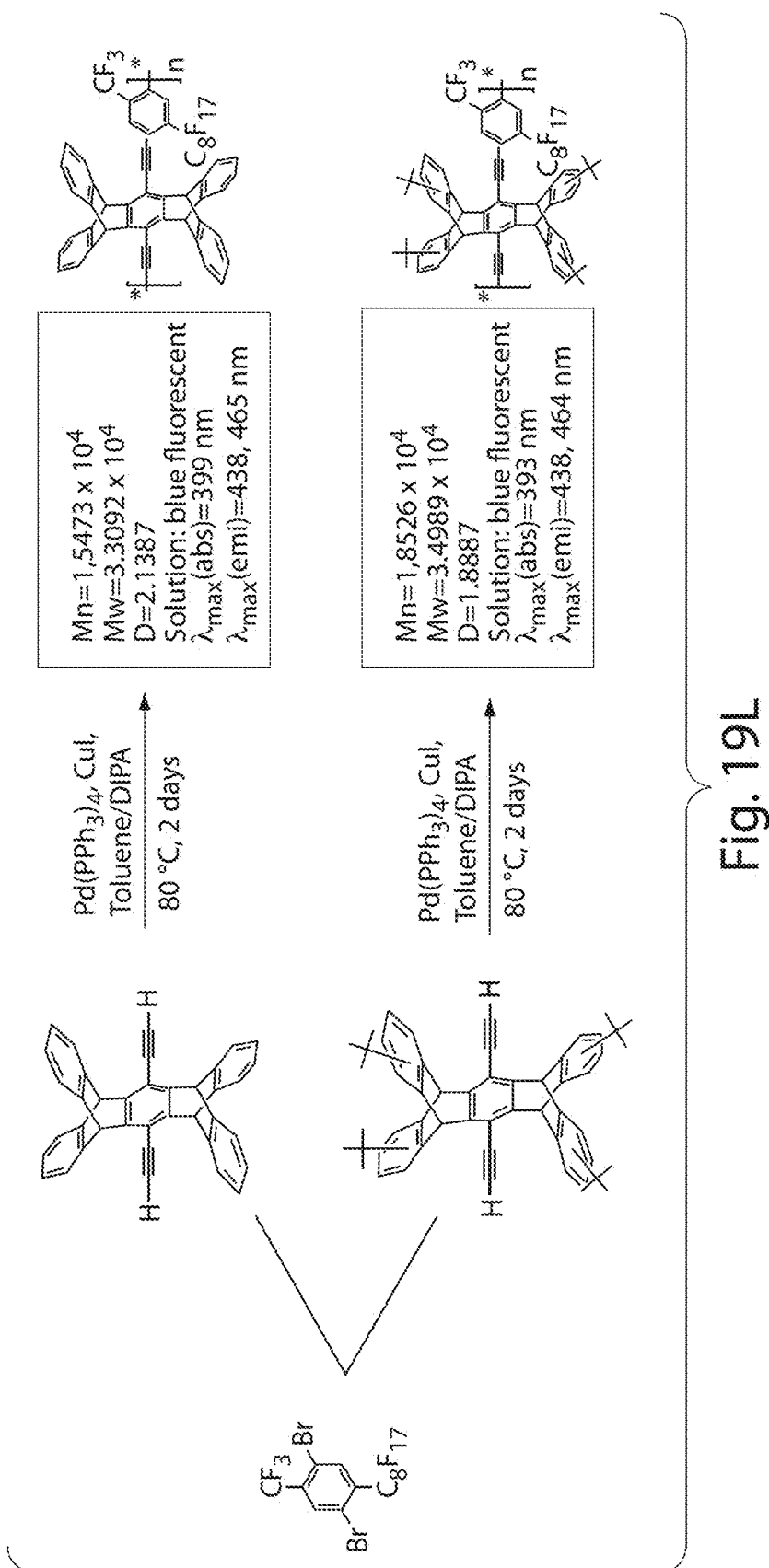


Fig. 19K



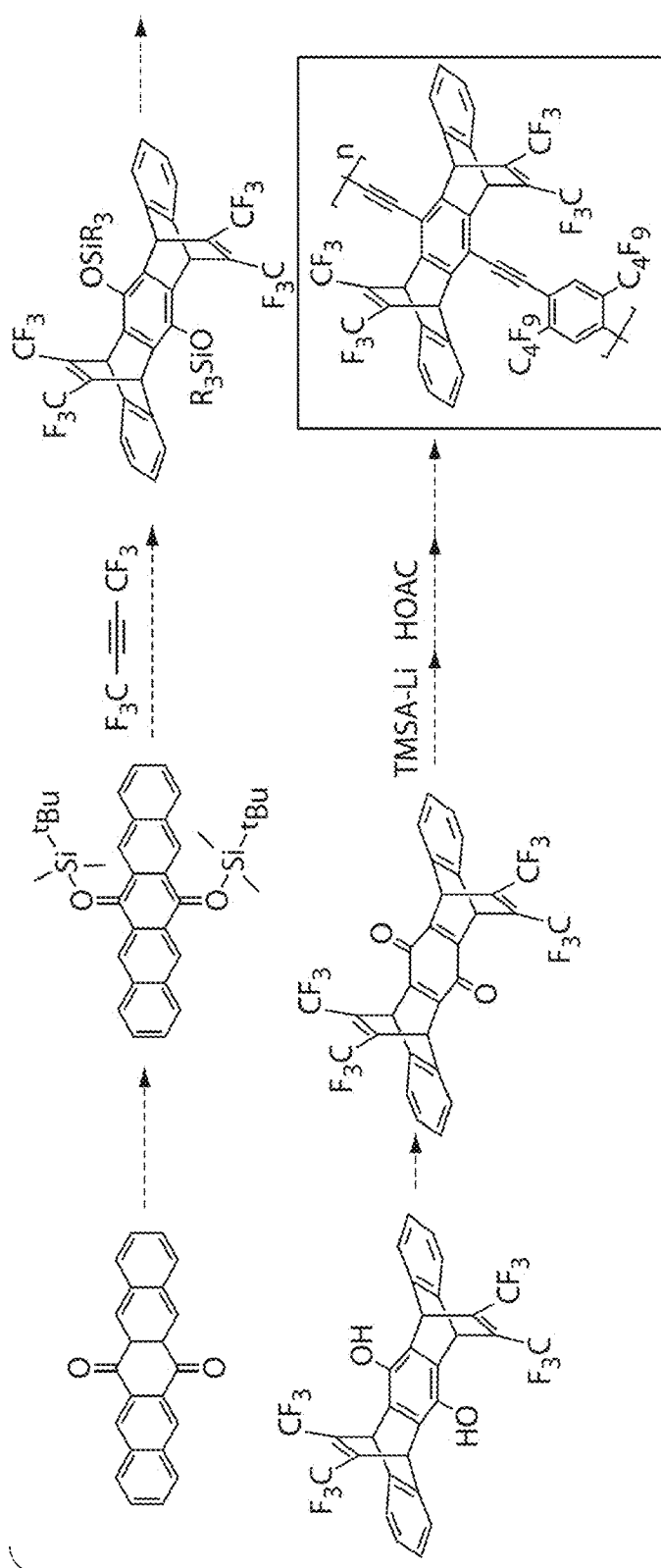


Fig. 1961

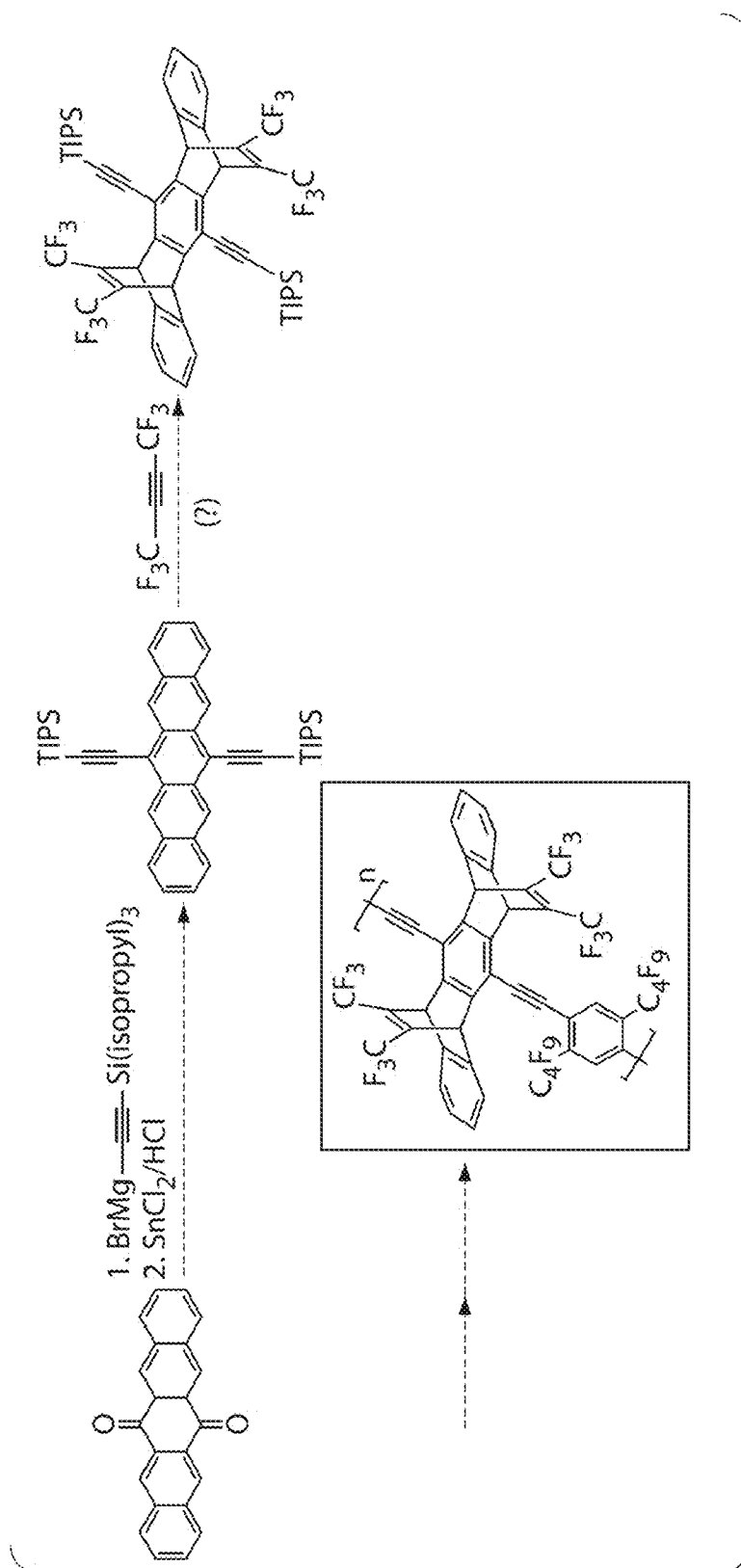


Fig. 19N

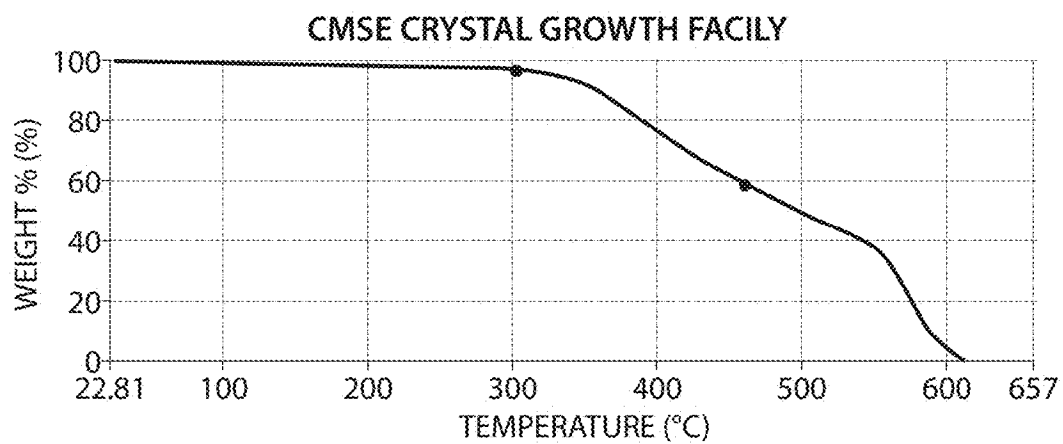


Fig. 20A

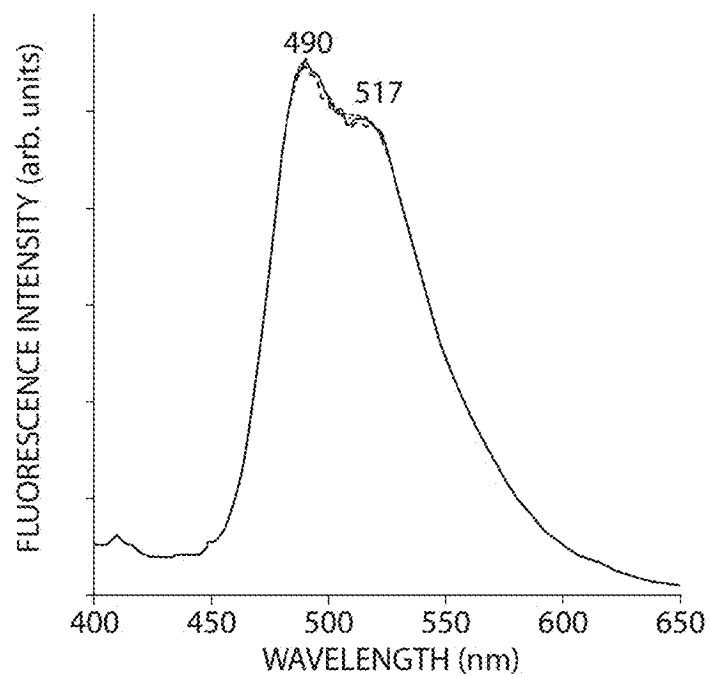


Fig. 20B

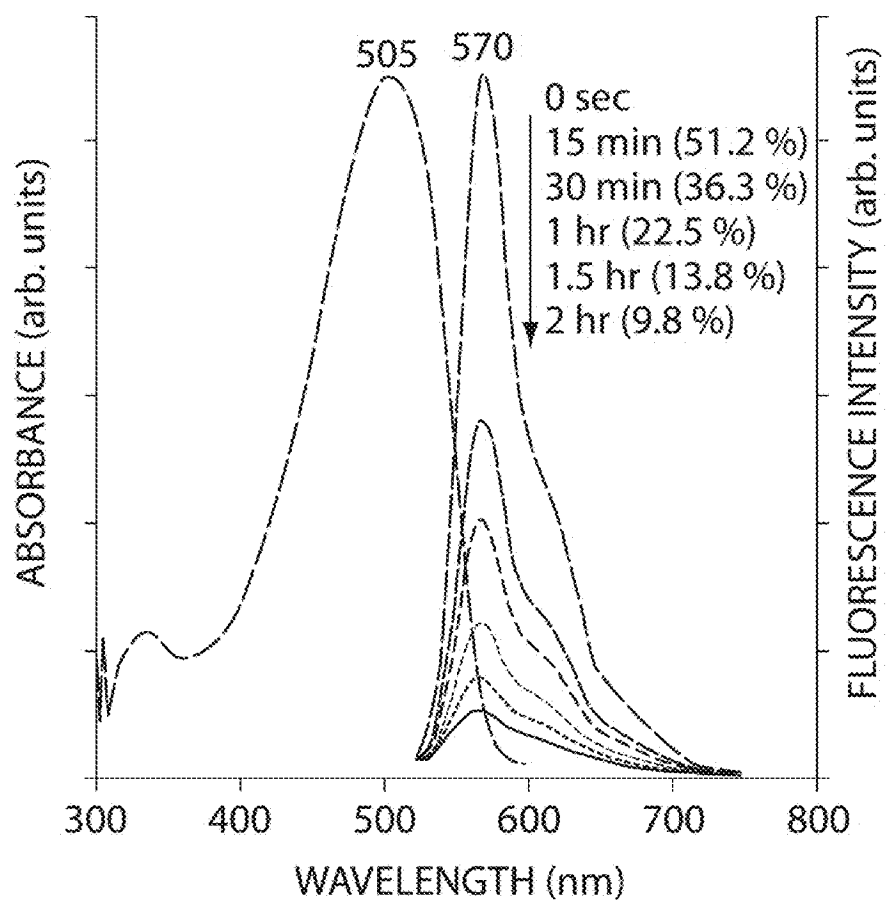


Fig. 20C

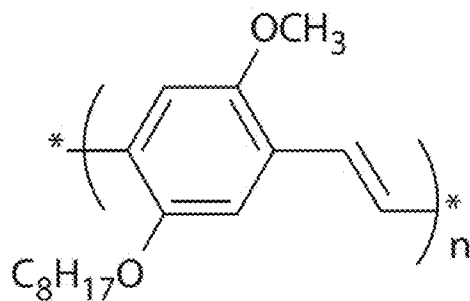


Fig. 20D



Fig. 21A

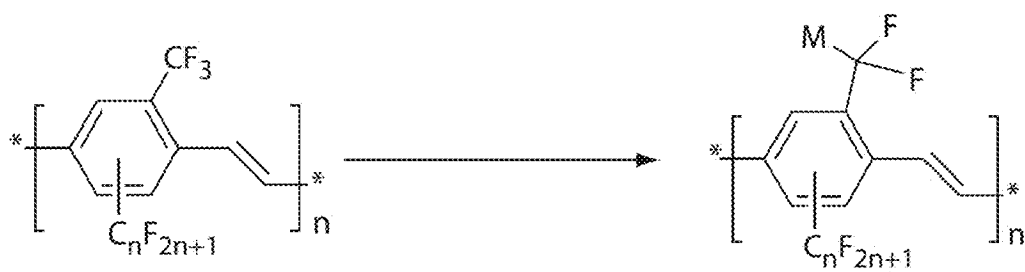


Fig. 21B

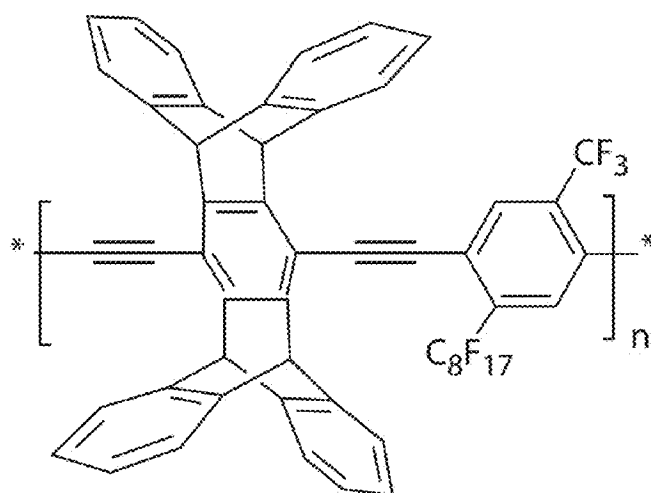


Fig. 22A

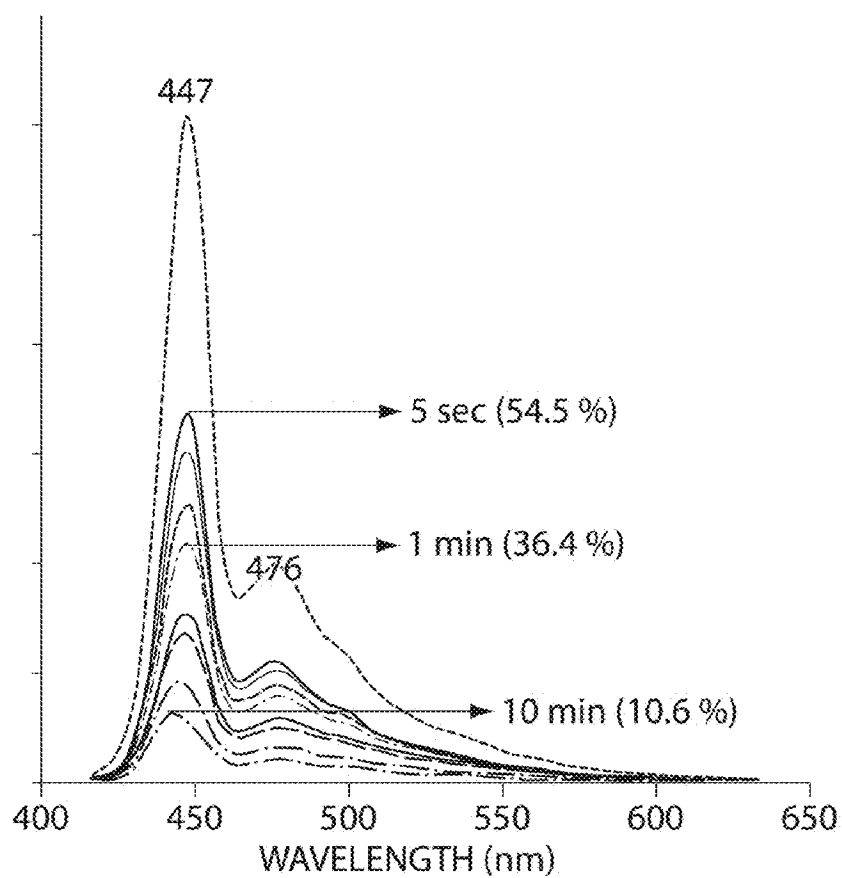


Fig. 22B



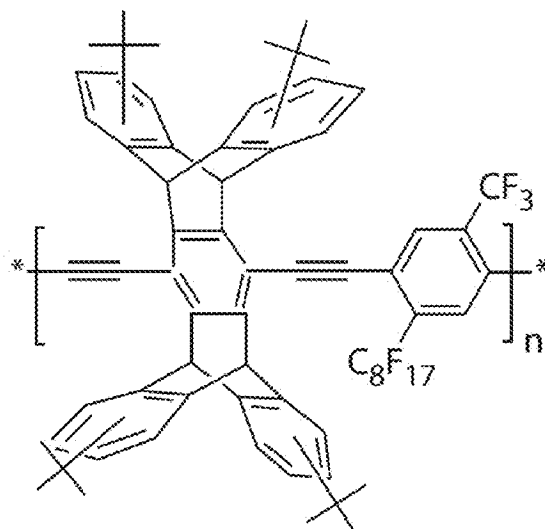


Fig. 22C

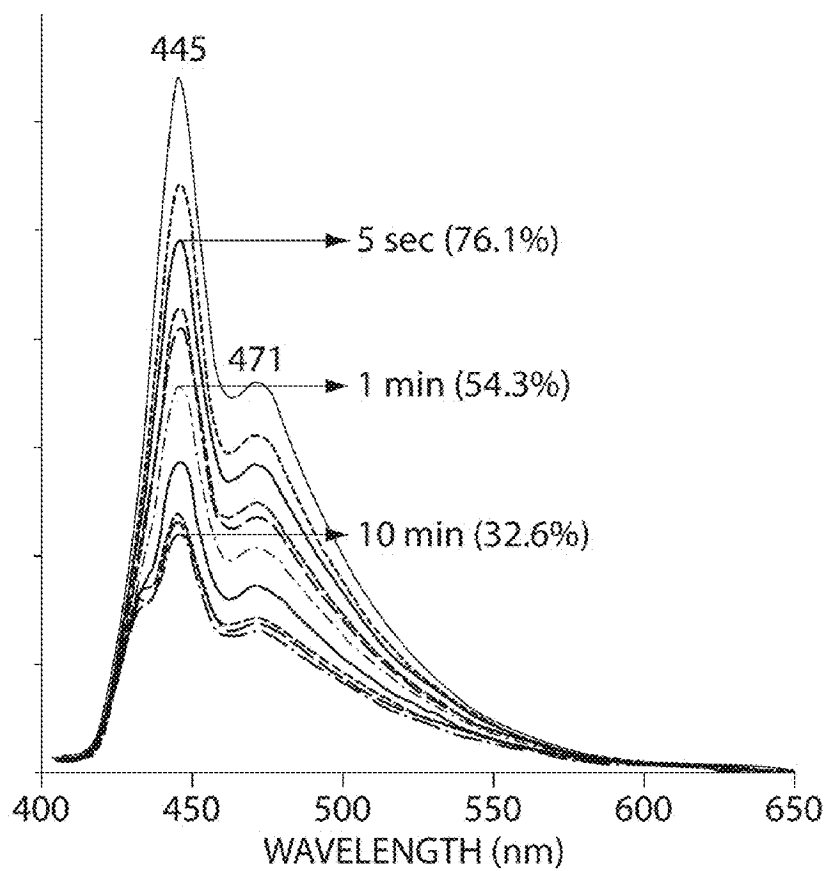


Fig. 22D

## ORGANIC MATERIALS ABLE TO DETECT ANALYTES

### RELATED APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 11/005,631, filed Dec. 6, 2004, entitled "Organic Materials Able To Detect Analytes," by Rose et al., which claims priority under 35 U.S.C. §119(e) to U.S. Provisional Patent Application Ser. No. 60/527,395, filed Dec. 5, 2003, entitled "Organic Materials Able To Detect Analytes," by Rose, et al, both of which applications are incorporated herein by reference in their entirety.

### FEDERALLY SPONSORED RESEARCH

This invention was made with government support under Contract Number 6891253, awarded by DARPA, and Grant No NAS2-02056, awarded by NASA. The government has certain rights in the invention.

### FIELD OF INVENTION

The present invention generally relates to polymers with lasing characteristics and, in particular, to polymers with lasing characteristics that allow the polymers to be useful in detecting analytes. In some cases, the polymers may be thermally, photochemically, and/or chemically stable in thin films. In certain instances, the polymers may be soluble in organic solvents. In one set of embodiments, the polymers comprise conjugated backbones and use electron withdrawing groups to affect the electron affinity of the polymers.

### BACKGROUND

Semiconducting organic polymers have emerged as important class of luminescent sensor materials due to their ability to self-amplify. Non-limiting examples of organic polymers that may be semiconductive are disclosed in the following: U.S. patent application Ser. No. 09/305,379, filed May 5, 1999, entitled "Emissive Polymers and Devices Incorporating These Polymers," by Swager, et al.; U.S. patent application Ser. No. 09/935,060, filed Aug. 21, 2001, entitled "Polymers with High Internal Free Volume," by Swager, et al.; and U.S. patent application Ser. No. 10/680,714, filed Oct. 27, 2003, entitled "Emissive Sensors and Devices Incorporating These Sensors," by Swager, et al. Each of these is incorporated herein by reference.

### SUMMARY OF THE INVENTION

The present invention generally relates to polymers with lasing characteristics that allow the polymers to be useful in detecting analytes. The subject matter of the present invention involves, in some cases, interrelated products, alternative solutions to a particular problem, and/or a plurality of different uses of one or more systems and/or articles.

One aspect of the invention provides a device. In one set of embodiments, the device is a device for detecting an analyte. In one embodiment, the device includes a polymer that, upon interaction with an analyte, exhibits a change in a lasing characteristic. The device also includes, in some cases, an energy source able to cause the polymer to lase.

In another aspect, of the invention, an article is provided. According to one set of embodiments, the article includes a polymer, that, upon interaction with an analyte, exhibits a change in a stimulated emission signal that is at least 10 times

greater than a change in a spontaneous emission signal of the polymer. In another set of embodiments, the article includes a polymer that, upon interaction with an analyte, exhibits a change in a lasing characteristic. In some cases, the polymer further includes a binding site for an analyte which, when it binds at the site, changes the lasing characteristic.

The invention, in yet another aspect, provides a method. The method, according to one set of embodiments, is a method of determining an analyte. The method, in one embodiment, includes acts of contacting a polymer with a sample suspected of containing an analyte, and determining a change in a lasing characteristic of the polymer indicative of the presence of the analyte in the sample. In another embodiment, the method includes acts of contacting a polymer with a sample suspected of containing an analyte, and determining a change in a stimulated emission signal of the polymer that is at least 10 times greater than a change in a spontaneous emission signal of the polymer indicative of the presence of the analyte in the sample.

In one set of embodiments, the polymer is fluorescent. The polymer may also be semiconductive in some cases. In one embodiment, the polymer comprises a conjugated backbone and one or more electron donating and/or electron withdrawing groups bonded to or otherwise associated with the polymer. For example, electron withdrawing groups may be bonded directly to the conjugated backbone, or bonded to the polymer, but not bonded directly to the conjugated backbone.

In another aspect, the present invention is directed to a method of making one or more of the embodiments described herein. In yet another aspect, the present invention is directed to a method of using one or more of the embodiments described herein. In still another aspect, the present invention is directed to a method of promoting one or more of the embodiments described herein.

Other advantages and novel features of the present invention will become apparent from the following detailed description of various non-limiting embodiments of the invention when considered in conjunction with the accompanying figures. In cases where the present specification and a document incorporated by reference include conflicting and/or inconsistent disclosure, the present specification shall control. If two or more documents incorporated by reference include conflicting and/or inconsistent disclosure with respect to each other, then the later-filed application shall control.

### BRIEF DESCRIPTION OF THE DRAWINGS

Non-limiting embodiments of the present invention will be described by way of example with reference to the accompanying figures, which are schematic and are not intended to be drawn to scale. In the figures, each identical or nearly identical component illustrated is typically represented by a single numeral. For the purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention. In the figures:

FIG. 1 is a schematic diagram of a fluorescence quenching mechanism;

FIG. 2 is a chemical structure of a polymer of an embodiment of the invention;

FIGS. 3A-3C are schematic diagrams of various planar lasing structures, in accordance with various embodiments of the invention;

FIG. 4 is a plot of emission intensity vs. input power, according to one embodiment of the invention;

FIGS. 5A-5B are plots of spectral responses of certain embodiments of the invention;

FIG. 6 is a spectral response plot of another embodiment of the invention;

FIG. 7 is a spectral response plot of yet another embodiment of the invention;

FIG. 8 is a schematic diagram of energy levels in an example of a conjugated polymer of the invention;

FIG. 9 is a schematic diagram showing laser power output vs. pumping power input, in accordance with an embodiment of the invention;

FIG. 10 is a plot of emission intensity vs. input power, in another embodiment of the invention;

FIG. 11 is a schematic diagram showing excitation of a polymer of one embodiment of the invention;

FIG. 12 is a schematic diagram of a detection system of an embodiment of the invention;

FIG. 13 is a schematic diagram of a detection system of another embodiment of the invention;

FIG. 14 is a schematic diagram of a charge transfer process in one embodiment of the invention;

FIGS. 15A-15G illustrate various perfluorinated alkyl PPVs potentially suitable for use in certain embodiments of the invention;

FIGS. 16A-16B illustrate the preparation of certain polymers potentially suitable for use in some embodiments of the invention;

FIGS. 17A-17D illustrate various Stern-Volmer plots of certain polymers of the invention;

FIGS. 18A-18B illustrate various emission spectra of certain polymers of the invention;

FIGS. 19A-19N illustrate certain reaction pathways useful for preparing certain polymers of the present invention;

FIGS. 20A-20D illustrate the analysis of trifluoromethyl substituted PPV and MEH-PPV, according to one embodiment of the invention;

FIGS. 21A-21B illustrate certain reaction pathways potentially suitable for use in the present invention; and

FIGS. 22A-22D illustrate certain results from indole quenching experiments on PPEs with perfluorinated alkyls bonded directly to a conjugated backbone, according to one embodiment of the invention.

### DETAILED DESCRIPTION

The present invention generally relates to polymers with lasing characteristics that allow the polymers to be useful in detecting analytes. In one aspect, the polymer, upon an interaction with an analyte, may exhibit a change in a lasing characteristic that can be determined in some fashion. For example, interaction of an analyte with the polymer may affect the ability of the polymer to reach an excited state that allows stimulated emission of photons to occur, which may be determined, thereby determining the analyte. In another aspect, the polymer, upon interaction with an analyte, may exhibit a change in stimulated emission that is at least 10 times greater with respect to a change in the spontaneous emission of the polymer upon interaction with the analyte. The polymer may be a conjugated polymer in some cases. In one set of embodiments, the polymer includes one or more hydrocarbon side chains, which may be parallel to the polymer backbone in some instances. In another set of embodiments, the polymer may include one or more pendant aromatic rings. In yet another set of embodiments, the polymer may be substantially encapsulated in a hydrocarbon. In still another set of embodiments, the polymer may be substantially resistant to photobleaching. In certain aspects, the poly-

mer may be useful in the detection of explosive agents, such as 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT).

The following documents are incorporated herein by reference: U.S. patent application Ser. No. 09/305,379, filed May 5, 1999, entitled "Emissive Polymers and Devices Incorporating These Polymers," by Swager, et al.; U.S. patent application Ser. No. 09/935,060, filed Aug. 21, 2001, entitled "Polymers with High Internal Free Volume," by Swager, et al., now U.S. Pat. No. 6,783,814, issued Aug. 31, 2004; U.S. patent application Ser. No. 10/324,064, filed Dec. 18, 2002, entitled "Emissive Polymers and Devices Incorporating These Polymers," by Swager, et al., published as 2003-0178607 on Sep. 25, 2003; U.S. patent application Ser. No. 10/680,714, filed Oct. 27, 2003, entitled "Emissive Sensors and Devices Incorporating These Sensors," by Swager, et al.; U.S. Provisional Patent Application Ser. No. 60/527,395, filed Dec. 5, 2003, entitled "Organic Materials Able To Detect Analytes," by Rose, et al.; and U.S. patent application Ser. No. 10/823,093, filed Apr. 12, 2004, entitled "Emissive Sensors and Devices Incorporating These Sensors," by Swager, et al.; U.S. patent application Ser. No. 10/764,768, filed Jan. 26, 2004, entitled "Polymers with High Internal Free Volume," Swager, et al.

In some embodiments, the polymer is provided in conjunction with a material defining a substantially non-light scattering optical medium which can interact optically with the polymer to cause light emission, changes in which can be caused by interaction of the polymer and/or the optical medium with an analyte. The light emitted may be substantially monochromatic, include a limited number of wavelengths (or "modes"), or the light may be emitted in a broad range of wavelengths. The polymer can be provided in conjunction with the medium by being in optical communication with the medium in some manner, for example, being positioned proximate the medium such that light can readily move between the polymer and the medium, or provided directly upon the medium itself. For example, the polymer can be provided as a thin layer on a surface of the optical medium, such as a substrate.

The substantially non-light scattering medium can be transparent to (i.e., not substantially scattered by) wave lengths of electromagnetic radiation of interest, that is, wavelengths at which emission occurs and can be changed by the presence of an analyte. The optical medium can be readily selected by those of ordinary skill in the art based upon the present disclosure from materials including silica, other glasses, polymers such as polycarbonate, or the like. In one embodiment, the optical medium provides optical feedback to the polymer, which acts as an emitter of light, sufficient to create amplified stimulated emission. In this case, the optical medium serves as a medium for the collection of light at a concentration high enough to provide amplified stimulated emission. Those of ordinary skill in the art will recognize and readily be able to select and construct combinations of polymers and optical media of dimension and geometry such that optical characteristics including amplified stimulated emission as described here and can occur. Where the optical medium provides feedback at selective modes, the optical medium alone and/or in combination with the polymer can define a laser.

A variety of definitions are now provided, which will aid in understanding various aspects of the invention. Following, and interspersed with these definitions, is additional disclosure that will more fully describe the invention.

The term "fluid," as used herein, is defined as a substance that tends to flow and to conform to the outline of its container. Typically, fluids are materials that are unable to with-

stand a static shear stress. When a shear stress is applied to a fluid, it experiences a continuing and permanent distortion. Typical fluids include liquids and gases.

As used herein, the term “determining” (and similar terms) generally refers to the measurement and/or analysis of a species, for example, quantitatively or qualitatively, and/or the detection of the presence or absence of the species. “Determining” may also refer to the measurement and/or analysis of an interaction between two or more species, for example, quantitatively or qualitatively, and/or by detecting the presence or absence of the interaction.

As used herein, the term “sample” refers to any medium that can be evaluated in accordance with the invention, such as air, soil, water, a biological sample, etc. A “sample suspected of containing” a particular component means a sample with respect to which the content of the component is unknown. For example, a soil sample may be suspected of having one or more explosive agents, but is not known to have the explosive agent. “Sample” in this context includes naturally-occurring samples, such as soil samples, water samples, air samples, samples from food, livestock, plants, etc.

As used herein, “binding” includes covalent binding, ionic binding, hydrogen binding, van der Waals interactions, metal ligand binding, dative binding, coordinated binding, hydrophobic interactions, or the like.

As used herein, “alkyl” is given its ordinary meaning as used in the field of organic chemistry. Alkyl (i.e., aliphatic) moieties useful for practicing the invention can contain any of a wide number of carbon atoms, for example, between and 1 and 25 carbon atoms, between 1 and 20 carbon atoms, between 1 and 15 carbon atoms, between 1 and 10 carbon atoms, or between 1 and 5 carbon atoms. In some embodiments, the alkyl moiety will contain at least 1 carbon atom, at least 3 carbon atoms, at least 5 carbon atoms, or at least 10 carbon atoms; in other embodiments, the alkyl moiety will have at most 10 carbon atoms, at most 5 carbon atoms, or at most 3 carbon atoms. The carbon atoms within the alkyl moiety may be arranged in any configuration within the alkyl moiety, for example, as a straight chain (i.e., a n-alkyl such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, etc.) or a branched chain, i.e., a chain where there is at least one carbon atom that is covalently bonded to at least three carbon atoms (e.g., a t-butyl moiety, an isoalkyl moiety such as an isopropyl moiety or an isobutyl moiety, etc.). In certain embodiments, a straight chain or branched chain alkyl has about 30 or fewer carbon atoms (e.g., C<sub>1</sub>-C<sub>30</sub> for straight chain, C<sub>3</sub>-C<sub>30</sub> for branched chain), in some cases, about 20 or fewer atoms, etc. The alkyl moiety may contain only single bonds (i.e., the alkyl is “saturated”), or may contain one or more double and/or triple bonds within its structure (i.e., the alkyl is “unsaturated”), for example, as in an alkene, an alkyne, an alkadiene, an alkadiyne, an alkenyne, etc.

In some cases, the alkyl moiety contains only carbon and hydrogen atoms; however, in other embodiments, the alkyl moiety may also contain one or more substituents, i.e., a non-carbon and non-hydrogen atom (“a heteroatom”) may be present within the alkyl moiety. Non-limiting examples of heteroatoms include halogens, boron, nitrogen, oxygen, phosphorus, sulfur, and selenium. For example, the alkyl moiety may include a halogen, an alkoxy moiety (e.g., methoxy or ethoxy), an amine moiety (e.g., a primary, secondary, or tertiary amine), a carbonyl (e.g., an aldehyde and/or a ketone), and/or a hydroxide as a substituent. If more than substituent is present within the alkyl moiety, then the substituents may each independently be the same or different. In one embodiment, an alkyl is a perhalogenated alkyl, as further discussed below.

An alkyl may be acyclic, or cyclic in some cases. Cyclic alkyls include, but are not limited to, cycloalkyl (alicyclic) moieties, aromatic moieties, aralkyl moieties, alkyl substituted cycloalkylmoieties, cycloalkyl substituted alkylmoieties, etc. Certain cycloalkyls may have from about 3 to about 10 carbon atoms in their ring structure, for instance, 5, 6, or 7 carbons in a ring structure.

An “aromatic” moiety is given its ordinary meaning as used in the art, i.e., a moiety having at least one ring in which some electrons are delocalized in the ring. For instance, the aromatic moiety may include a benzene moiety, a naphthalenyl moiety, an anthracenyl moiety, a pyridinyl moiety, a furanyl moiety, etc. Examples of aromatic compounds include, but are not limited to, nitroaromatics such as 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), nitrotoluene, etc. Other non-limiting examples of aromatics that are of biological or environmental importance include, but are not limited to, dioxin, dopamine, aniline, benzene, toluene, and phenols.

The term “aryl” is art-recognized, and includes 5-, 6- and 7-membered single-ring aromatic groups that may include from zero to four heteroatoms, for example, benzene, pyrrole, furan, thiophene, imidazole, oxazole, thiazole, triazole, pyrazole, pyridine, pyrazine, pyridazine and pyrimidine, and the like. Those aryl groups having heteroatoms in the ring structure may also be referred to as “heteroaryls.” The aromatic ring may be substituted at one or more ring positions with such substituents as described above, for example, halogen, azide, alkyl, aralkyl, alkenyl, alkynyl, cycloalkyl, hydroxyl, alkoxy, amino, nitro, sulfhydryl, imino, amido, phosphonate, phosphinate, carbonyl, carboxyl, silyl, ether, alkylthio, sulfonyl, sulfonamido, ketone, aldehyde, ester, heterocyclyl, aromatic or heteroaromatic moieties, —CF<sub>3</sub>, —CN, or the like. The term “aryl” also includes polycyclic ring systems having two or more cyclic rings in which two or more carbons are common to two adjoining rings (the rings are “fused rings”) wherein at least one of the rings is aromatic, e.g., the other cyclic rings may be cycloalkyls, cycloalkenyls, cycloalkynyls, aryls and/or heterocyclyls. Similarly, the term “aralkyl” is art-recognized, and includes alkyl groups substituted with an aryl group (e.g., an aromatic or heteroaromatic group).

The terms “heterocyclyl” and “heterocyclic group” are art-recognized, and, in some cases, include 3- to 10-membered ring structures, such as 3- to 7-membered rings, for example, whose ring structures include one to four heteroatoms. Heterocycles may also be polycycles in some cases. Heterocyclyl groups include, for example, thiophene, thianthrene, furan, pyran, isobenzofuran, chromene, xanthene, phenoxathiin, pyrrole, imidazole, pyrazole, isothiazole, isoxazole, pyridine, pyrazine, pyrimidine, pyridazine, indolizine, isoindole, indole, indazole, purine, quinoline, isoquinoline, quinoline, phthalazine, naphthyridine, quinoxaline, quinoxaline, cinnoline, pteridine, carbazole, carboline, phenanthridine, acridine, pyrimidine, phenanthroline, phenazine, phenarsazine, phenothiazine, furazan, phenoxazine, pyrrolidine, oxolane, thiolane, oxazole, piperidine, piperazine, morpholine, lactones, lactams such as azetidinones and pyrrolidinones, sultams, sultones, and the like. The heterocyclic ring may be substituted at one or more positions with such substituents as described above, as for example, halogen, alkyl, aralkyl, alkenyl, alkynyl, cycloalkyl, hydroxyl, amino, nitro, sulfhydryl, imino, amido, phosphonate, phosphinate, carbonyl, carboxyl, silyl, ether, alkylthio, sulfonyl, ketone, aldehyde, ester, a heterocyclyl, an aromatic or heteroaromatic moiety, —CF<sub>3</sub>, —CN, or the like.

The definition of each expression, e.g. alkyl, m, n, etc., when it occurs more than once in any structure, is intended to

be independent of its definition elsewhere in the same structure unless otherwise indicated expressly or by the context.

A “polymer,” as used herein, is an extended molecular structure comprising a backbone which optionally contains pendant side groups, where “backbone” generally refers to the longest continuous bond pathway of the polymer. Those of ordinary skill in the art will be able to identify the backbone of a polymer. In one embodiment, the polymer includes one or more polyarylenes, polyarylene vinylenes, polyarylene ethylenes, and/or ladder polymers, i.e. polymers having a backbone that can only be severed by breaking two bonds. Examples of such polymers include, but are not limited to, polythiophene, polypyrrole, polyacetylene, polyphenylene and substituted derivatives thereof.

Non-limiting examples of polymers suitable for the invention include those disclosed in U.S. patent application Ser. No. 09/305,379, filed May 5, 1999, entitled “Emissive Polymers and Devices Incorporating These Polymers,” by Swager, et al.; U.S. patent application Ser. No. 09/935,060, filed Aug. 21, 2001, entitled “Polymers with High Internal Free Volume,” by Swager, et al.; and U.S. patent application Ser. No. 10/680,714, filed Oct. 27, 2003, entitled “Emissive Sensors and Devices Incorporating These Sensors,” by Swager, et al, each incorporated herein by reference. Other examples of polymers suitable for the invention are described in more detail herein.

The polymer is, in some cases, a homo-polymer or a co-polymer, such as a random co-polymer or a block co-polymer. In one embodiment, the polymer is a block co-polymer. An advantageous feature of block co-polymers is that the effect of a multi-layer can be mimicked. For example, each block may have different band gap components, and by nature of the chemical structure of a block co-polymer, each gap component may be segregated in some embodiments. Thus, amplified emissions can be achieved with block co-polymers, and a broad scope of structures can be produced, according to certain embodiments of the invention. Band gaps, amplifications and selectivities for analytes can thus be achieved by modification or incorporation of different polymer types. The polymer compositions can vary continuously to give a tapered block structure, according to some embodiments, and the polymers can be synthesized by methods known to those of ordinary skill in the art, such as step growth, chain growth, or the like.

One aspect of the present invention provides a polymer capable of emission, wherein the emission may be variable and sensitive to a dielectric constant of a surrounding medium. In some cases, the polymer is semiconductive. In one set of embodiments, the polymer has a backbone including a plurality of chromophores, which may be interrupted by non-conjugated groups in some cases. Non-conjugated groups include, for example, saturated units such as a chain of alkyl groups optionally interrupted by heteroatoms. A “chromophore,” as used herein, refers to a species that can either absorb or emit electromagnetic radiation. In some embodiments, the chromophore is capable of absorbing or emitting radiation in the ultraviolet and/or visible range, i.e. absorbing or emitting energy involving excited electronic states. In one embodiment, the chromophore is a conjugated group. As used herein, a “conjugated group” refers to an interconnected chain of at least three atoms, each atom participating in delocalized pi-bonding.

In another set of embodiments, at least a portion of the polymer is conjugated, i.e. the polymer has one or more conjugated portions. For example, in one embodiment, the polymer backbone includes at least one conjugated group. In the conjugated portion, electron density and/or electronic

charge can be conducted along that portion, and such electron density and/or electronic charge may be referred to as being “delocalized.” Within the conjugated portion, each p-orbital participating in the conjugation may have sufficient overlap with adjacent conjugated p-orbitals. In one embodiment, the conjugated portion is at least about 3 nm in length and in some cases, the conjugated portion is at least about 5 nm, at least about 10 nm, at least about 15 nm, at least about 25 nm, or more in length. In another embodiment, the entire backbone, or substantially all of the entire backbone, is conjugated and the polymer is referred to as a “conjugated polymer,” i.e., the entire polymer, or substantially all of the entire polymer, is the “conjugated portion.” Polymers having a conjugated backbone capable of conducting electronic charge along the backbone are typically referred to herein as “conducting polymers.” In the present invention, the conducting polymers may comprise, in some cases, chromophore monomeric units, or chromophores interspersed between other conjugated groups. In certain cases, the atoms directly participating in the conjugation essentially define a plane, which may arise from a preferred arrangement of the p-orbitals to maximize p-orbital overlap, thus maximizing conjugation and electronic conduction. An example of a conjugated-backbone defining essentially a plane of atoms are the carbon atoms of a polyacetylene chain.

In one embodiment, a polymer is provided having a conjugated backbone defining essentially a plane of atoms. A first group of atoms and a second group of atoms are attached to the backbone of the polymer. Both the first and second groups have at least some atoms that are not planar with the plane of atoms, such that the atoms can be positioned above and/or below the conjugated plane of atoms. It is a feature of certain embodiments of the invention that these heights are fixed, where the term “fixed height” is defined herein as a height of an atom that is not planar with the plane of atoms, and where the atom is free of substantial rotational motion.

In another embodiment, the present invention relates to a polymer comprising a conjugated backbone and one or more electron donating and/or electron withdrawing groups associated with the polymer, for example, bonded to the polymer.

The polymer may comprise, in some cases, one or more electron withdrawing groups, where a portion of the electron withdrawing group is directly bonded to the conjugated backbone, and/or the polymer may comprise one or more electron withdrawing groups that are not bonded directly to the backbone. For example, in some embodiments, the polymer comprises a first moiety where the electron withdrawing group is not bonded directly to the backbone, and a second moiety where the electron withdrawing group is bonded directly to the conjugated backbone. The term “electron-withdrawing group” is art-recognized, and generally refers to the tendency of a substituent to attract valence electrons from neighboring atoms, i.e., the substituent is electronegative with respect to neighboring atoms. In some cases, quantification of the level of electron-withdrawing capability may be given by the Hammett sigma ( $\sigma$ ) constant. This constant is described in many references, for instance, March, *Advanced Organic Chemistry*, 251-59 (McGraw Hill Book Company: New York, 1977). The Hammett constant values are generally negative for electron donating groups (e.g.,  $\sigma(\text{P})$  or  $\sigma(\text{P})=-0.66$  for  $\text{NH}_2$ ) and positive for electron withdrawing groups (e.g.,  $\sigma(\text{P})$  or  $\sigma(\text{P})=0.78$  for  $\text{NO}_2$ ). Examples of electron-withdrawing groups include, but are not limited to, halogenated alkyl groups such as trifluoromethyl, acyl, formyl, sulfonyl, sulfonium, sulfate, nitrile, halide, any electron deficient ring as compared to benzene (e.g. a benzene ring with an electron withdrawing group attached to the ring or a nitrogen contain-

ing aromatic ring, etc.), or the like. In some embodiments, the electron withdrawing groups are not bonded directly to the conjugated backbone, and in certain instances, the polymer may have a hyperconjugated 3-D structure. Other non-limiting examples of electron withdrawing groups include esters, perhalogenated alkyls, perhalogenated aryls, nitriles, electron deficient heteroaryls, perfluorinated alkyls, or the like. Non-limiting examples of perfluorinated alkyls include perfluorinated C<sub>1</sub>-C<sub>12</sub> alkyls; specific examples include —CF<sub>3</sub>, —C<sub>2</sub>F<sub>5</sub>, —C<sub>3</sub>F<sub>7</sub>, —C<sub>4</sub>F<sub>9</sub>, —C<sub>5</sub>F<sub>11</sub>, —C<sub>6</sub>F<sub>13</sub>, —C<sub>7</sub>F<sub>15</sub>, —C<sub>8</sub>F<sub>17</sub>, —C<sub>9</sub>F<sub>19</sub>, —C<sub>10</sub>F<sub>21</sub>, —C<sub>11</sub>F<sub>23</sub>, etc. and all isomers thereof. For example, a polymer may be substituted with fluorinated alcohol groups for hydrogen bonding with weak hydrogen bonded acceptors such as nitro groups. In some cases, electron-poor polymers, for example, produced through the use of electron withdrawing groups, can enable quenching by electron-rich analytes and thus, in one embodiment, sensors having specificity for electron-rich analytes are provided. Sensitivity to electron-rich analytes can be achieved, in some cases, by substituting a polymer with groups that increase electron affinity, such as electron withdrawing groups.

Certain perfluorinated alkyls may provide a higher degree of solubility than the analogous polymers of equal chain length hydrocarbon substituents, according to some embodiments of the invention. In some cases, the perfluorinated alkyls may prevent strong interpolymer interactions, and in some instances, thin films of these materials may maintain fluorescence while in the solid state. The high electron affinity of the perfluorinated alkyls, in some embodiments, may complement other sensor materials, e.g., as described herein.

The polymer may be fluorescent and/or semiconductive in some cases. The term “fluorescence” is art-recognized and generally refers to the emission of electromagnetic radiation caused by an electronic transition from an excited electronic state of a given spin to a lower energy electronic state. In yet another embodiment, the present invention includes conjugated polymers that produce high fluorescence quantum yields. In some cases, the polymer can also be used to tune electron affinity. Architectures are provided herein for the covalent attachment of the conjugated polymers to peptides, nucleic acids, antibodies, etc., e.g., for biosensor applications that avoid deleterious reductions in their electronic delocalization. In some cases, conjugated polymers having three-dimensional structures that display efficient solid-state fluorescence may be used, and hyperconjugation can be used to tune electron affinities of the polymers. In one embodiment, multiple conjugated polymers having different electronic properties due to strongly electron withdrawing groups directly attached to their backbones may be used.

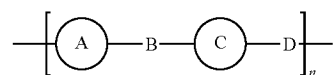
Semiconductive polymers having electron withdrawing substituents directly attached to conjugated portions of the polymers are provided in another embodiment of the invention. For example, semiconductive polymers containing perfluorinated alkyl groups, or other electron withdrawing groups, may have a relatively high electron affinity that prevents oxidative degradation (photobleaching). The term “photobleaching” is art-recognized, and refers to the decrease in absorbance intensity upon exposure to light and/or, in the case of fluorescent materials, a decrease in emission intensity. The perfluorinated alkyl polymers disclosed herein are generally stable after one or more hours of irradiation with UV light (e.g. a 450 W, short-arc, Xe lamp) in solid state, under ambient atmosphere.

Polymers having hydrogen-bonding capabilities can also be synthesized, according to other embodiments of the invention. For example, in one embodiment, the invention provides

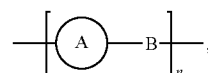
the ability to detect analytes capable of hydrogen-bonding interactions. In another embodiment, the polymer is soluble in an organic solvent.

In some embodiments of the invention, the polymers may be present in a composition that is rigid with respect to the relative orientation between the polymers. In one embodiment, the compositions of the present invention are rigid to the extent that the polymer arrangement does not substantially change over time, upon exposure to solvent or upon heating to a temperature of no more than about 150° C. That is, the rigidity of the side group defining a fixed height may not substantially change and the height may not be affected upon heating. In one embodiment, the exposure to solvent or heating step occurs over a period of time of about 5 minutes, about 10 minutes, about 15 minutes, about 30 minutes, or about 1 hour. In one embodiment, the composition is characterized by a first optical spectrum having at least one maximum or maxima. The composition is then exposed to a solvent or heated to a temperature of less than about 140° C. and a second optical spectrum is obtained. A maximum or maxima in the first spectrum differ by no more than about 15 nm from a corresponding maximum or maxima in the second spectrum, and in some cases, by no more than about 10 nm or about 5 nm. In another embodiment, the maxima in the second spectrum may have an intensity change of less than about 10%, or about 15% relative to the maxima in the first spectrum.

In one set of embodiments, the polymer has a structure:

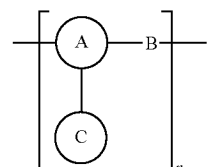


where n is at least 1, A and C are each independently aromatic, and at least one of B and D comprises a —C=C— structure (i.e., a double bond) or —C≡C— structure (i.e., a triple bond). In another set of embodiments, the polymer has a structure:



where n is at least 1, A is aromatic, and B comprises a —C=C— structure (i.e., a double bond) or —C≡C— structure (i.e., a triple bond).

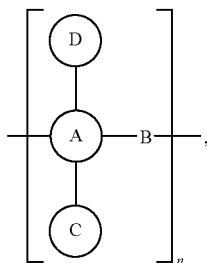
In some embodiments, the polymer may include one or more pendant aromatic groups. The pendant aromatic groups may increase the optical cross-section of the polymer, which may enhance absorption efficiency and/or emission efficiency in some cases. In one set of embodiments, the polymer has a structure:



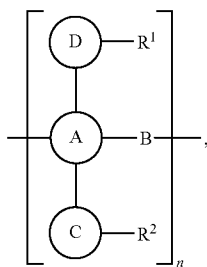
where n is at least 1, A and C are each independently aromatic, and B comprises a —C=C— structure (i.e., a double bond)

## 11

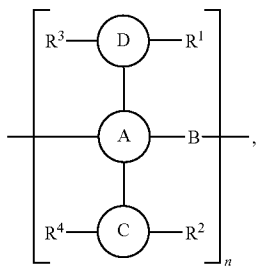
or  $\text{—C}\equiv\text{C—}$  structure (i.e., a triple bond). In another set of embodiments, the polymer has a structure:



where  $n$  is at least 1, A, C, and D are each independently aromatic; and B comprises a  $\text{—C}=\text{C—}$  structure (i.e., a double bond) or  $\text{—C}\equiv\text{C—}$  structure (i.e., a triple bond). In another set of embodiments, the polymer has a structure:



where  $n$  is at least 1, A, C, and D are each independently aromatic; B comprises a  $\text{—C}=\text{C—}$  structure (i.e., a double bond) or  $\text{—C}\equiv\text{C—}$  structure (i.e., a triple bond), and each of  $R^1$  and  $R^2$  independently comprises a hydrocarbon, as further discussed herein. In yet another set of embodiments, the polymer has a structure:



where  $n$  is at least 1, A, C, and D are each independently aromatic, B comprises a  $\text{—C}=\text{C—}$  structure (i.e., a double bond) or  $\text{—C}\equiv\text{C—}$  structure (i.e., a triple bond), and each of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  independently comprises a hydrocarbon. In the above structures,  $n$  may be, for example, at least 2, at least 3, at least 5, at least 10, at least 30, at least 100, at least 300, at least 1,000, at least 3,000, at least 10,000, at least 100,000, or at least 1,000,000. In one embodiment,  $n$  is less than  $10^8$ .

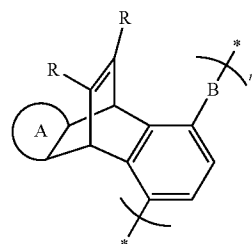
In some embodiments, the polymer includes one or more hydrocarbon side chains substantially parallel to the backbone of the polymer, i.e., the side chains may substantially

## 12

parallel the 3-dimensional structure of the backbone (which may or may not be linear). In some cases, one or more pendant groups may be used to secure the hydrocarbon side chains in an orientation such that they are substantially parallel to the backbone of the polymer. As used herein, a “hydrocarbon” is a moiety comprising at least carbon and hydrogen, and in some cases, the hydrocarbon comprises heteroatoms such as oxygen, nitrogen, sulfur, etc. In one embodiment, the hydrocarbon is an alkyl moiety, which may be straight or branched.

In another set of embodiments, the polymer may be substantially surrounded by hydrocarbon. For example, a hydrocarbon may sufficiently surround the polymer to reduce interaction of the polymer with adjacent polymer molecules such that the polymers, for instance, so that the polymer molecules cannot substantially quench each other. As another example, the hydrocarbon may sufficiently surround the polymer such that the ability of  $\text{O}_2$  or radicals to interact with the polymer is reduced. As yet another example, the hydrocarbon may sufficiently surround the polymer such that the polymer is not photobleached, i.e., after exposure to light for long periods of time, the polymer does not substantially lose its lasing abilities.

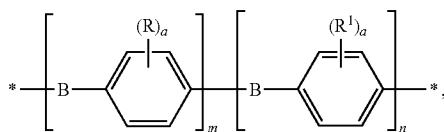
In another set of embodiments, the polymer has a structure:



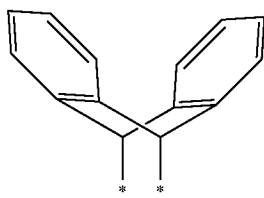
where, independently for each occurrence, R is an electron donating and/or electron withdrawing group or the two instances of R taken together form an electron deficient ring; B is a double bond, triple bond, or aryl group substituted by one or more  $R_1$ ;  $R_1$  is R, H,  $\text{C}_{1-12}$  alkyl,  $\text{C}_{2-12}$  alkenyl,  $\text{C}_{2-12}$  alkynyl, aryl, aralkyl, heteroaryl, or heteroaralkyl; A is a fused aryl, cycloalkyl, or cycloalkenyl ring; \* depicts an end group for the polymer, for example, H, halide, alkyl, alkoxy, and aryl; and  $n$  is an integer greater than 1. In some cases, R may be an ester, a perhalogenated alkyl group, a perfluorinated alkyl group (for example, a  $\text{C}_{1-12}$  perfluorinated alkyl group),  $\text{—CO}_2\text{CH}_3$ ,  $\text{—CO}_2\text{C}(\text{CH}_3)_3$ . Examples of perfluorinated alkyl group include, but are not limited to,  $\text{—CF}_3$ ,  $\text{—C}_2\text{F}_5$ ,  $\text{—C}_3\text{F}_7$ ,  $\text{—C}_4\text{F}_9$ ,  $\text{—C}_5\text{F}_{11}$ ,  $\text{—C}_6\text{F}_{13}$ ,  $\text{—C}_7\text{F}_{15}$ ,  $\text{—C}_8\text{F}_{17}$ ,  $\text{—C}_9\text{F}_{19}$ ,  $\text{—C}_{10}\text{F}_{21}$ ,  $\text{—C}_{11}\text{F}_{23}$ , etc. In certain embodiments, at least one set of two R groups taken together form an electron deficient heteroaryl moiety. In some cases, A may be a fused benzene ring. In some embodiments,  $n$  is greater than about 10, about 100, about 1,000, about 10,000, or about 100,000. In one embodiment,  $n$  is less than about  $10^8$ . As a particular example, R may be  $\text{—CO}_2\text{CH}_3$  or  $\text{—CF}_3$ ,  $R_1$  may be H, A may be a fused benzene ring, and  $n$  may be greater than about 10, 100, 1000, etc.

In yet another set of embodiments, the polymer has a structure:

13



where, independently for each occurrence, B is a double bond, triple bond, or aryl; R is an electron donating and/or electron withdrawing group; R<sup>1</sup> is R, H, C<sub>1-6</sub> alkyl, C<sub>2-8</sub> alkenyl, C<sub>2-8</sub> alkynyl, aryl, aralkyl, heteroaryl, heteroaralkyl, C<sub>1-12</sub> alkoxy, electron deficient ring, or any two adjacent R<sup>1</sup> taken together form a monocyclic, bicyclic, tricyclic, or tetracyclic ring which may be substituted by 1 or more R; \* depicts an end group for the polymer selected from the group consisting of H, halide, alkyl, alkoxy or aryl; a is an integer from 1-4 inclusive; and m and n are integers 1 or greater. The polymer may be, for example, a random polymer, a block polymer, an alternating polymer, etc. In some cases, R may be an ester, a perhalogenated alkyl group, a perfluorinated alkyl group (for example, a C<sub>1-12</sub> perfluorinated alkyl group), —CO<sub>2</sub>CH<sub>3</sub>, —CO<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>. Examples of perfluorinated alkyl group include, but are not limited to, —CF<sub>3</sub>, —C<sub>2</sub>F<sub>5</sub>, —C<sub>3</sub>F<sub>7</sub>, —C<sub>4</sub>F<sub>9</sub>, —C<sub>5</sub>F<sub>11</sub>, —C<sub>6</sub>F<sub>13</sub>, —C<sub>7</sub>F<sub>15</sub>, —C<sub>8</sub>F<sub>17</sub>, —C<sub>9</sub>F<sub>19</sub>, —C<sub>10</sub>F<sub>21</sub>, —C<sub>11</sub>F<sub>23</sub>, etc. In certain embodiments, at least one set of two R groups taken together form an electron deficient heteroaryl moiety. In some cases, at least one or at least two of R<sup>1</sup> is a perfluorinated C<sub>1-12</sub> alkyl or a C<sub>1-12</sub> alkoxy group. In some cases, a may be 2 or more, and in certain instances, m and n may independently be greater than about 10, about 100, about 1,000, about 10,000, about 100,000, etc., and in one embodiment, less than about 10<sup>8</sup>. In one embodiment, two sets of adjacent R<sup>1</sup> each form a monocyclic ring, a bicyclic ring, a tricyclic ring, or a tetracyclic ring. In some cases, at least one structure comprises a heteroaryl ring. For example, in one embodiment, two sets of R<sup>1</sup> each may form a structure:



where \* depicts a point of contact with the polymer.

Additional, non-limiting examples of polymers suitable for use in the present invention are shown in FIGS. 15A-15G.

In one set of embodiments, the polymer may be present in a film. A film typically has a geometry such that one dimension is substantially less than the other dimensions (i.e., the “thickness” of the material may be substantially less than the other dimensions of the material). In some cases, the thickness of the film may affect the sensitivity of the polymer. For example, the film have a thickness of less than about 1 micron, and in some cases, the film may have a thickness of less than about 750 nm, less than about 600 nm, less than about 500 nm, less than about 400 nm, less than about 200 nm, less than about 100 nm, less than about 40 nm, less than about 30 nm, less than about 20 nm, less than about 10 nm, less than about 5 nm, or less than about 2 nm. In one embodiment, the film has a thickness of at least 1 nm.

14

In one embodiment, the film is attached to a substrate, which may serve as an optical medium in some cases. The film may be attached to the substrate using any suitable technique, for example, spin-coating techniques. The substrate may have any shape, and include any material able to support the film. For example, the substrate may be substantially planar or curved, the substrate may be a rod, a wire, or a fiber (for example, a silica fiber), the substrate may comprise discrete particles (e.g., spherical particles), etc. In some embodiments, e.g., as shown in FIG. 3, more than one substrate may be present. As a non-limiting example, a glass substrate may be coated with a film of parylene, then a film of polymer may be coated on the parylene. In FIG. 3, FIG. 3A shows a polymer waveguide on a glass substrate, and FIG. 3B shows a thin polymer layer on parylene. The combined thickness of polymer and parylene may act as a waveguide. FIG. 3C shows a thin polymer layer on a DFB grating, which may significantly reduces the lasing threshold in some cases.

In some cases, the film and the substrate together operate as a waveguide, e.g., as is shown in FIG. 3A. In such cases, the refractive index of the film and the refractive index of the substrate may be chosen such that they are nearly or substantially equal. In some instances, one of the substrate and/or film may be doped in some fashion to match the refractive index of the other. In some cases, one or more of the substrates may be at least substantially transparent, e.g., to the excitation and/or emission wavelengths, and/or optically.

In one embodiment, the substrate has the form of a distributed feedback structure (“DFB”) or a distributed feedback grating or other structure. As used herein, a “distributed feedback” structure is given its ordinary meaning in the art, e.g., a structure in which feedback is used to make certain modes in the resonator oscillate more strongly than others. The structure may include a grating (e.g., a Bragg grating) having a spacing chosen to distribute the feedback in both directions, creating a condition that can approach single-mode oscillation, as is shown in FIG. 3C. Those of ordinary skill in the art will know of techniques for producing distributed feedback structures, for example, by using micromolding techniques.

Other substrates may be used in other embodiments of the invention. For example, in one set of embodiments, the polymer (or film comprising the polymer) may be attached to or otherwise associated with a non-light scattering optical medium. Examples of non-light scattering optical medium include, but are not limited to, silica, other glasses, polymers such as polycarbonate, or the like. In another set of embodiments, the non-light scattering optical medium includes an optical fiber. For example, the polymer may be at least partially coated on a surface of the optical fiber (for example, as a film). An interaction of the polymer with an analyte may cause the polymer to alter an optical characteristic of the optical fiber. For example, if the optical fiber is used as a laser, then the interaction may cause the polymer to alter a lasing characteristic of the optical fiber. The non-light scattering optical medium, in some embodiments, may carry or “collect” photons, and, through the use of a feedback mechanism (for example, a distributed feedback structure), may create selective modes for lasing, for example through amplified stimulated emission.

In one aspect, the present invention generally relates to polymers able to generate amplified stimulated emission of electromagnetic radiation, i.e., a laser, and devices such as sensors able to detect analytes which incorporate these polymers, e.g., in films. As used herein, a “laser” is given its ordinary meaning, i.e., an article able to emit amplified and coherent electromagnetic radiation having one or more discrete frequencies, typically in response to an electrical or an



optical stimulus (e.g., incident light, or "stimulation" light). The article, when it exhibits such behavior, is said to "lase." The emitted light may have any frequency or wavelength, for example, in the ultraviolet, visible, or infrared wavelengths. Within the laser, atoms may be excited into a metastable "excited" energy state (for example, due to electrical or optical stimulation), such that these excited atoms decay to a lower energy level, releasing photons. Thus, a coherent beam of radiation may be produced within the laser. Any suitable lasing mechanism may be used within the invention. In one aspect of the invention, the ability of the polymer to reach a metastable excited energy state may be affected by the interaction or association of an analyte with the polymer.

In one set of embodiments, the polymer is able to produce coherent light under certain conditions. In some cases, the polymer may exhibit an enhanced lasing characteristic. As used herein, a "lasing characteristic" is a characteristic of the polymer that relates to the ability of the polymer to enter a metastable excited energy state. Examples of lasing characteristics include, but are not limited to, the "lasing threshold" (i.e., the minimal amount of incident stimulation needed for the polymer to reach a metastable excited energy state, for example, the minimal amount of energy, light (photon) intensity, etc.), the stimulated emission (i.e., the amount of energy produced by the polymer, relative to a fixed standard, such as spontaneous emission), the gain (i.e., the relative amount of energy or photons emitted by the laser, relative to the amount of incident energy), etc.

In one set of embodiments, interaction of an analyte with the polymer may alter a lasing characteristic of the polymer. For example, lasing of the polymer may increase or decrease upon interaction of the polymer with the analyte. In some cases, interaction of the analyte with the polymer may change (i.e., increase or decrease) stimulated emission of the polymer, relative to spontaneous emission of the polymer, and such a change may be detectable in some fashion, as described herein. In some cases, the relative change between stimulated emission of the polymer, relative to spontaneous emission of the polymer may be at least a factor of 5 times, and in some cases, at least a factor of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 200, 400, 600, 800, 1,000, or more.

In some embodiments, the laser is an electrically-driven laser. In other embodiments, the laser may be "optically-driven" to generate amplified stimulated emission of radiation. As used herein, "optically-driven" refers to components powered by an external optical or electromagnetic radiation source. In an optically-driven device, electromagnetic radiation is directed towards a material (such as a polymer) where the atoms are to be excited. The electromagnetic radiation source may be any suitable source, for example, a flash tube, a diode, or another laser. In yet other embodiments, the laser may include a waveguide or an amplifier.

In one embodiment, the polymer has a quantum yield of at least about 50%, at least about 60%, at least about 70%, at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, or at least about 97%. As used herein, the "quantum yield" refers to a number of photons emitted per adsorbed photon of a material (such as a polymer). In some cases, the quantum yield is determined at a wavelength of electromagnetic radiation produced by the power source.

In some embodiments, the analyte, upon association with the polymer, introduces a non-radiative pathway in the polymer, which may attenuate lasing. In some cases, an electron transfer event from the excited state of the polymer to the LUMO of the analyte provides non-radiative decay pathway for the exciton, e.g., as is shown in FIG. 1. Thus, association

of the analyte to the polymer may result in a change in the lasing properties of the polymer, and such a change may be determinable.

One aspect of the invention provides a sensor comprising one or more of the polymers described herein. A "sensor," as used herein, refers to any device or article capable of determining an analyte, i.e., a molecule which is to be determined. In one embodiment, the analyte comprises an aromatic moiety. In another embodiment, the analyte is an "explosive agent," i.e., an agent able to detonate. Examples of explosive agents include, but are not limited to 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT), nitroglycerine, gunpowder, etc. Other non-limiting examples include RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), PETN (2,2-bis[(nitrooxy)-methyl]-1,3-propanediol dinitrate (ester)) and nitroaromatics and other nitro-(NO<sub>2</sub>) containing species, as further described herein. The sensor may determine the absolute value and/or a change in a physical or chemical quantity, such as temperature, pressure, flow rate, or pH, the intensity of light, sound, or radio waves, the presence of a small molecule, the presence of a biological molecule, a change in a characteristic of a bound molecule, or the like, and convert that determination into a useful input signal for an information gathering system. For instance, in one set of embodiments, the polymer exhibits a change in a lasing characteristic upon interaction of the polymer with an analyte. The interaction between the polymer and the analyte may be, e.g., through covalent binding, ionic binding, hydrogen binding, van der Waals interactions, metal ligand binding, dative binding, coordinated binding, hydrophobic interactions, etc. In one embodiment, the polymer ceases to lase upon interaction of the polymer with the analyte. In another embodiment, the polymer begins to lase upon interaction of the polymer with the analyte. In yet another embodiment, the lasing threshold of the polymer may increase or decrease upon interaction of the polymer with the analyte.

In one set of embodiments, the present invention relates to a sensor comprising a polymer as described herein, and a detector capable of detecting an increase or a decrease in fluorescence. In some cases, the sensor is a biosensor. In certain cases, the polymer and the analyte may be optically coupled. The term "optically coupled" when used herein with reference to a polymer and an analyte, or other moiety such as a reaction entity, refers to an association between any of the analyte, other moiety, and the polymer such that energy can move from one to the other, or in which a change in the association can be detected by a change in a lasing characteristic of the polymer. The coupling between the analyte and the polymer may be direct or indirect (i.e., through a linking agent).

In one set of embodiments, the polymer inherently includes the ability to determine the analyte. The polymer may be functionalized in some cases, e.g., comprising pendant groups, functional moieties, linking agents associated with binding partners, etc., to which the analyte may bind and induce a measurable change to the polymer. The binding event can be specific or non-specific. The functional moieties may include simple functional groups, for example, but not limited to, —OH, —CHO, —COON, —SO<sub>3</sub>H, —CN, —NH<sub>2</sub>, —SH, —COSH, —COOR, a halide, etc.; and/or biomolecular entities including, but not limited to, amino acids, proteins, sugars, DNA, antibodies, antigens, enzymes, or the like.

In another set of embodiments, the invention provides a polymer and a reaction entity with which the analyte interacts, positioned in relation to the polymer such that the analyte can be determined by determining a change in a charac-

teristic of the polymer, for example, a lasing characteristic. The term "reaction entity" refers to any entity that can interact with an analyte in such a manner to cause a detectable change in characteristic of a polymer. For example, the reaction entity may enhance the interaction between the polymer and the analyte, the reaction entity may generate a new chemical species that has a higher affinity to the polymer, the reaction entity may enrich the analyte around the polymer, or the like. The reaction entity can comprise a binding partner to which the analyte binds in some cases. The reaction entity, when a binding partner, may also comprise a specific binding partner of the analyte. For example, the reaction entity may be a nucleic acid, an antibody, a sugar, a carbohydrate, a protein, etc. A reaction entity that is a catalyst can catalyze a reaction involving the analyte in some instances, resulting in a product that causes a detectable change in a characteristic of the polymer. Another example of a reaction entity is a reactant that reacts with the analyte, which may produce a product that can cause a detectable change in a characteristic of the polymer. The reaction entity can comprise a coating on the polymer in some embodiments, e.g. a coating of a polymer that recognizes molecules in, e.g., a gaseous sample, which may cause a change in conductivity of the polymer which, in turn, can cause a detectable change in a characteristic of the polymer.

The term "binding partner," as used herein, refers to a molecule that can undergo binding with a particular analyte and includes specific, semi-specific, and non-specific binding partners, as known to those of ordinary skill in the art. As used herein the term "specifically binds," when referring to a binding partner (e.g., protein, nucleic acid, antibody, etc.), refers to a reaction that is determinative of the presence and/or identity of one or other member of the binding pair in a mixture of heterogeneous molecules (e.g., proteins and other biologics). Thus, for example, in the case of a receptor/ligand binding pair, the ligand would specifically and/or preferentially select its receptor from a complex mixture of molecules, or vice versa. For example, an enzyme would specifically bind to its substrate, a nucleic acid would specifically bind to its complement, an antibody would specifically bind to its antigen, etc. Other non-limiting examples include nucleic acids that specifically bind (hybridize) to their complement, antibodies specifically bind to their antigen, or the like. The binding may be by one or more of a variety of mechanisms including, but not limited to, ionic interactions, covalent interactions, hydrophobic interactions, van der Waals interactions, etc.

Thus, in one set of embodiments, the present invention relates to a method of determining an analyte that is a biological molecule. In one embodiment, the biological molecule is a protein. In another embodiment, the biological molecule is a peptide. In yet another embodiment, the biological molecule is a mono- or oligonucleotide. In a further embodiment, the biological molecule is RNA. In still another embodiment, the biological molecule is DNA. In another embodiment, the biological molecule is determined when it complexes with another peptide molecule, small molecule, RNA, or DNA.

The reaction entity may be positioned, in some embodiments, relative to the polymer in such a way as to cause a determinable change in a lasing characteristic of the polymer. For instance, the reaction entity may be positioned within about 100 nanometers of the polymer, within about 50 nanometers of the polymer, within about 10 nanometers of the polymer, etc., and the proximity of the reaction entity to the polymer can be determined by those of ordinary skill in the art. In another embodiment, the reaction entity is positioned

less than about 5 nanometers from the polymer. In alternative embodiments, the reaction entity is positioned within about 4 nanometers, within about 3 nanometers, within about 2 nanometers, or within about 1 nanometer of the polymer. In one embodiment, the reaction entity is attached to the polymer through a linker. In another embodiment, the polymer itself (or a portion thereof) functions as the reaction entity.

Another set of embodiments of the invention involves an article comprising a sample exposure region and a polymer able to detect the presence or absence of an analyte. The sample exposure region may be any region in close proximity to the polymer where a sample in the sample exposure region addresses at least a portion of the polymer. Examples of sample exposure regions include, but are not limited to, a well, a channel, a microchannel, a gel, or the like. In some embodiments, the sample exposure region holds a sample proximate the polymer, and/or may direct a sample toward the polymer for determination of an analyte in the sample. The polymer may be positioned adjacent to or within the sample exposure region. In other cases, the polymer may be a probe that is inserted into a fluid or fluid flow path. The polymer probe may also comprise a microneedle, and the sample exposure region may be addressable by a biological sample in certain instances. In this arrangement, a device that is constructed and arranged for insertion of a microneedle probe into a biological sample may include a region surrounding the microneedle defining the sample exposure region, and a sample in the sample exposure region may be addressable by the polymer, and vice versa. Fluid flow channels can be created at a size and scale advantageous for use in the invention (microchannels) using a variety of techniques, such as those described in International Patent Publication No. WO 97/33737.

In yet another set of embodiments, an article may comprise a plurality of polymers as described herein able to detect the presence or absence of a plurality of one or more analytes. Different polymers may be differentially doped in some cases, as described above, thereby varying the sensitivity of the polymers to the analyte. Different polymers may also be selected based on their ability to interact with specific analytes in other cases, thereby allowing the determination of a variety of analytes. The plurality of polymers may be arranged in any suitable configuration, for example, randomly oriented, parallel to one another, etc. In one embodiment, the polymers may be oriented in an array on a substrate.

One aspect of the invention involves a sensing element, which can be a sensing element for determining a characteristic of a polymer such as a lasing characteristic, for example, where the polymer has determined the presence, or absence, of an analyte in a sample containing, or suspected of containing, the analyte. Sensors comprising the polymers of the invention may be used, for example, in chemical or environmental applications to detect explosive agents or other analytes of interest. In some cases, the sample size is less than or equal to about 10 microliters, in some cases less than or equal to about 1 microliter, and in some cases less than or equal to about 0.1 microliter. The sample size may be as small as about 10 nanoliters or less in still other cases.

The sensor also may include, in some cases, a source of energy applicable to the polymeric composition to cause stimulated radiation emission. The energy can include optical stimulation (e.g., a laser), electromagnetic radiation, electrical energy, chemical energy, etc. In some instances, the energy is of a frequency that can be absorbed by the polymer to create a metastable excited energy state, resulting in stimulated emission of radiation. The sensor also includes, in some

cases, a device for detecting the emission, such as, but not limited to, a photomultiplier, a photodiode or a charge coupled device.

Where a detector is present, any detector capable of determining characteristic, such as a lasing characteristic, associated with the polymer can be used. The concentration of a species, or analyte, may be detected using the detector from molar concentrations to micromolar concentrations, nanomolar concentrations, or less in some instances. In some cases, sensitivity can be extended to a single molecule. Thus, in one embodiment, an article of the invention is capable of delivering a single analyte molecule to the polymer, and the detector is constructed and arranged to determine a signal resulting from the interaction of the molecule with the polymer.

In another aspect, the present invention relates to a light emitting device (for example, a laser) comprising a polymer as described herein, and a source of electrical current comprising electrodes capable of supplying the polymer with electrons. In some embodiments, the polymer comprises perfluorinated alkyls and/or perfluorinated aryls, and in certain cases, at the interface between the electrodes and the polymer, metal-carbon bonds are formed. For example, the polymer may comprise perfluorinated alkyls and/or perfluorinated aryls, and at the interface between the electrode and the polymer, metal-fluoride complexes may be formed. In another example, the polymer comprises a nitrogen-containing electron-deficient heteroaryl, and at the interface between the electrode and the polymer, metal-nitrogen bonds are formed. In still another example, the polymer comprises a nitrogen-containing electron-deficient heteroaryl and a perfluorinated alkyl and/or a perfluorinated aryl, and at the interface between the electrode and the polymer, metal-carbon bonds, metal-nitrogen bonds and/or metal-fluoride bonds may be formed.

The following examples are intended to illustrate certain embodiments of the present invention, but do not exemplify the full scope of the invention.

#### EXAMPLE 1

This example demonstrates that attenuation of lasing action in a chemically-sensitive, optically-pumped polymer thin film can be a sensitive probe for detecting airborne analytes. The change in the lasing response can be over 100-fold more pronounced than the attenuation of the spontaneous emission response, which may increase the detection sensitivity by a comparable factor. In this example, sensitivity gains were demonstrated in detection of explosive vapors such as 2,4,6-trinitrotoluene ("TNT") and 2,4-dinitrotoluene ("DNT"). Both TNT and DNT introduced non-radiative pathways in the polymer thin film, which attenuated lasing. The increased optical losses upon analyte detection resulted in the cessation of the lasing action. The sensitivity enhancement can be very pronounced for lasing polymer films pumped at intensities near the lasing threshold. Additionally, this example illustrates the development of a TNT-sensitive polymer with relatively high thin film quantum yields of >85% and relatively high optical damage thresholds. This example also shows low lasing thresholds of about 185 nJ/cm<sup>2</sup> for 30 nm thick polymer films in ambient atmosphere, and about 30 nJ/cm<sup>2</sup> thresholds for similar films deposited on substrates patterned with distributed feedback gratings. The sensitivity gains via the lasing mechanism produced enhanced sensitivity for fast detection of trace analytes such as explosive vapors.

Semiconducting organic polymers are an important class of luminescent sensor materials due to their ability to self-amplify. Their signal gain has its origins in the facility of these

materials to transport excitons, which allows the short-lived excited states to visit a multitude of potential analyte binding sites. The detection of 2,4,6-trinitrotoluene and 2,4-dinitrotoluene using semiconductor polymer thin films enables the detection of buried landmines based on an explosive vapor signature. DNT is a synthetic byproduct of the manufacture of TNT and is often present in landmines containing TNT. The vapor pressure of DNT is much higher (about 100 ppb) than TNT (about 5 ppb). Thus, in some cases, DNT can be used to detect a buried mine even though it is less than 10% of the explosive component of a buried landmine. In TNT/DNT detection, the signal, fluorescence quenching is the result of the interaction between these nitroaromatic compounds (TNT or DNT), an electron-deficient pi-acid, and an electron-rich semiconductive polymer (FIG. 1). This quenching of emission may be the result of causing the polymer to reach ground state i.e., TNT/DNT charge transfer complexes may give rise to non-radiative states within the band gap, and electron-transfer from the organic polymer excited state to a bound TNT/DNT state. In some cases, rapid back-electron transfer may return the polymer to its ground state.

In this example, polymer 5 of FIG. 2 was used to demonstrate a lasing amplification scheme in SOPs ("semiconductive organic polymers"). Schematic diagrams of the experimental apparatus used in this example are shown in FIGS. 11-13. Polymer 5 is generally photophysical, stable, and is also sensitive to TNT and DNT, as discussed in this example. Its thin film luminescence spectrum peaks at  $\lambda$  (lambda)=505 nm and has a radiative lifetime of  $\tau$  (tau)=650 ps. The rapid radiative relaxation contributes to its high fluorescence efficiency in spun-cast thin films of  $\Phi$  (Phi)=85%, measured by comparison to a standard of 9,10-diphenylanthracene in PMMA ( $\Phi$  (Phi)=83%). The pendant aromatic rings were designed into this system to increase the optical cross-section, which may enhance both the absorption and emission efficiency. The specific substitution pattern of the pendant rings was chosen to bias the orientation of the hydrocarbon side chains parallel to the polymer backbone. The backbone of polymer 5 was effectively encapsulated in hydrocarbon, thereby preventing strong interpolymer associations that typically lower the emission efficiencies. Furthermore, the resistance of polymer 5 to photobleaching can be attributed to this protective sheath of hydrocarbon chains. The extended pi-orbital interactions in polymer 5 created a band structure that can facilitate exciton transport. Diffusion lengths of about 100 Å (angstroms) have also been measured.

The lasing action was generated by optically exciting thin films of polymer 5 with a 4 ns long nitrogen laser pulses ( $\lambda$  (lambda)=337 nm) at an operating frequency of 30 Hz. The beam was focused into a 9 by 0.9 mm stripe, and emission collected at a 60° angle from the excitation beam, which was incident normal to the substrate. All experiments were performed in air.

Simple asymmetric waveguides (FIG. 3A) were formed by spin casting thin films of polymer 5 from 50 mg/mL hexane solution onto glass substrates, with film thickness ranging from about 300 Å (angstroms) to about 4000 Å (angstroms). For films thicker than about 500 Å (angstroms), a multimode amplified stimulated emission (ASE) peaked at  $\lambda$  (lambda)=535 nm, coinciding with the first vibronic transition (0,1) of polymer 5. The selective emission from this mode may be governed by the reabsorption of the (0,0) emission within the thin films.

Given that the exciton diffusion length normal to the film surface can be estimated to an order of 100 Å (angstroms), for sensitivity in a TNT/DNT sensory device, film thicknesses of the order of about 100 Å (angstroms) may be needed in some